

Review

The $H^+ + H_2$ reaction

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H_3^+ plays a crucial role in Astrophysics, taking part in the early chemistry responsible for the formation of the stars. It is also one of the most abundant ionic species in hydrogen plasmas. The spectroscopy of the system has been the subject of intensive work in the past. Association processes to form H_3^+ and dissociative recombination with electrons have been also investigated in detail in order to understand the observed abundance of the molecule in the interstellar medium. Besides all these questions, in this work, we review some of the most relevant aspects regarding the dynamics of the $H^+ + H_2$ reaction and its isotopic variants. A discussion on the most commonly found numerical difficulties in the theoretical study of this reactive collision is included.

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1. Introduction

Given its relevance in Astrophysics, H_3^+ has been the subject of numerous investigations. Astronomy, dynamics and spectroscopy of this molecule are sufficiently important issues themselves to constitute separate reviews. The abundance of this ionic species, its participation in the early steps to form prestellar cores or in charge

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transfer reactions made some authors to refer to H_3^+ as an independent chapter in Chemistry.

Besides all efforts to measure and to obtain its spectrum, a great deal of work has been done in the past to estimate the abundance of H_3^+ in the interstellar medium and planetary atmospheres. In this sense, the $\text{H}^+\text{+H}_2$ association reaction to form the molecule and the dissociative recombination with low energy electrons which lead to its fragmentation play a crucial role. Both processes are considered in Section 4.

The *ortho-to-para* ratio (OPR) of H_2 has been found to be important in the cooling rates of small protogalactic objects colliding with molecular hydrogen. One of the most effective mechanisms to change the *ortho-para* character of H_2 is by means of the $\text{H}^+\text{+H}_2$ reaction. The relevance of the process in an astrophysical context is analyzed in Section 3.2.

This review makes a special emphasis on the dynamics of the $\text{H}^+\text{+H}_2$ reaction and its isotopic variants. According with previous investigations the reaction proceeds at some energy ranges via the formation of an intermediate complex. It is thus possible to establish some connections between this scattering species formed between reactants and products and the quasi-bound states existing in the high energy regime of the H_3^+ predissociation spectrum. A detailed overview of the most recent research regarding the relevant dynamical features of the reaction is included in Section 5.

Despite the vast list of existing studies on the subject, this work does not contain any explicit reference to preceeding work to calculate potential energy surfaces (PESs) of the H_3^+ system. The interested reader is referred however to the recent review by Lique *et al.* [1]. Suffice it to say for the scope of this review that most of the theoretical investigations on the reaction carried out by the authors employed PESs from References [2–4].

2. Spectroscopy

After its first experimental detection by Thompson [5, 6], H_3^+ soon became the target of intense spectroscopic investigation [7, 8]. The molecule does not have allowed rotational spectrum due to the absence of: (i) stable electronically excited states (with the sole exception of a triplet state close to the second dissociation limit) and (ii) a permanent dipole (due to the equilateral triangle equilibrium geometry [9]). The ν_2 vibration is the only accessible route to probe spectroscopically H_3^+ since excitations of the totally symmetric ‘breathing’ mode ν_1 do not change the zero dipole. The doubly degenerate asymmetric stretch/bend ν_2 , on the contrary, has a transition dipole of 0.23 Debye and the associated vibrational-angular motion l_2 .

The first detection of the H_3^+ spectrum was reported by Oka [10], with the assignment of 15 lines of the fundamental $\nu_2(l = \pm 1) \leftarrow 0$ band within the 2950–2450 cm^{-1} region. The observed pattern indicated a large interaction between vibration and rotation [8]. The vibrational-rotational spectrum of the isotopic variant D_3^+ was originally analysed between 1750–1850 cm^{-1} [11].

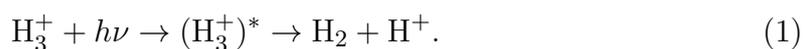
This experimental work was preceded by theoretical studies as the pioneering *ab initio* investigations of the vibrational spectra of H_3^+ [12] and deuterated species [13] performed by Carney and Porter. These authors predicted the frequency of the ν_2 -

fundamental band, 2516 cm^{-1} , which only differs about 5 cm^{-1} of the real value.

Later work included [14] not only the fundamental band but also overtones involving larger values of the total angular momentum J . Thus there were soon reports of more observed absorption lines in the ν_2 band with $J \leq 10$ [15, 16], and of the $2\nu_2$ band covering the $4500\text{--}5100\text{ cm}^{-1}$ region [17] with *ab initio* calculations for the corresponding line assignments extended up to $J = 12$. At the beginning of the 90s the laboratory spectroscopic information was completed with results on the $\nu_1 \leftarrow 0$ [18], $\nu_2 \leftarrow 0$ [18–21], $3\nu_2(1) \leftarrow 0$ overtone [22] and $\nu_1 + \nu_2 \leftarrow \nu_2$ bands [18]. A similar progress was made in the cases of D_3^+ [23–25], H_2D^+ [24, 26–31] and D_2H^+ [23, 24, 32, 33].

A more recent comprehensive list was presented by Lindsay and McCall [34] including studies performed in the following decade [35–40].

The low energy regime of the H_3^+ spectrum was completed with investigations up to $10000\text{--}16000\text{ cm}^{-1}$, close to the barrier to linearity of the system [41–49]. The trend of the investigations was to approach the near dissociation range investigated by Carrington and coworkers [23, 24, 50, 51]. In these works the predissociation spectra of H_3^+ , formed via the electron-impact ionization of H_2 , was analyzed after the photodissociation of the complex with a CO_2 laser according to:



A dense spectrum of about 27000 lines was observed over the $874\text{--}1094\text{ cm}^{-1}$ energy range. No regular features, apart of four distinct peaks close to the frequencies calculated for the $j' = 5 \leftarrow j = 3$ rotational transitions in the first four vibrational $v = 0 - 3$ manifolds of H_2 , were seen.

The possibility of finding quasibound states with lifetimes of microseconds above the dissociation limit of constituted an unexpected and challenging feature. The observed variation of the line widths was interpreted as evidence supporting predissociation as the pathway for the decomposition of the excited states. As Carrington and Kennedy pointed out [24], these predissociation quasibound states were consistent with interpretations of the $\text{H}^+ + \text{H}_2$ reaction in terms of an intermediate collision complex. Both the excess of internal energy and the long lifetimes of the H_3^+ ion observed in their experiments agreed with a complex-forming mechanism in the corresponding ion-diatom reaction.

First attempts to understand the spectrum of the molecular ion close to its dissociation limit considered the interaction of a proton H^+ with molecular hydrogen in its ($v = 2, j = 3$) state and a semiclassical treatment to analyse the existing resonances [52]. Classical tunnelling theory calculations suggested the existence of horseshoe states, also for nonzero total angular momentum, as responsible of the coarse grained spectrum at high energies [53]. Applications of such classical approaches [54] to study the metastability of H_3^+ followed by full quantum mechanical (QM) models to characterise its near-dissociation spectrum [55]. The main difficulties are related with the floppiness of the system, with very anharmonic vibrational modes and rapid distortions caused by centrifugal forces as the molecule is rotationally excited [56]. In addition, as expected for a very light molecule, individual rovibrational transitions for a specific vibrational manifold are widely spaced.

Recent investigations on the quasibound states of the H_3^+ species and isotopic variants [57] have continued the complex absorbing potential calculations by Mandelsham and Taylor [58]. The high-lying vibrational spectrum for low values of the total angular momentum, $J = 0 - 3$, has thus been investigated in different studies [59, 60].

3. Astrophysical interest

3.1. Presence in Space

The importance of the H_3^+ ion in the interstellar medium (ISM) comes both from its ability as proton donor for neutral species:



and from the role played to introduce D^+ instead of H^+ into the ion-molecule reaction sequence following the isotopic substitutions processes:



both exothermic, by 232 K and 509 K, respectively.

The first detection of H_3^+ in Space came from investigations on Jupiter [8]. Evidences for the existence of energetic molecular hydrogen, H_2^+ and H_3^+ [61] were inferred from data obtained in the Voyager 2 mission. In addition, an accidental observation was reported by Trafton *et al.* [62], who were primarily interested on the H_2 emission from the Jovian ionosphere. Their results showed a feature at 2093 μm corresponding to a transition from the $2 \nu_2(2) \rightarrow 0$ overtone band of H_3^+ . Almost simultaneously emission lines associated to H_3^+ between 4500-5000 cm^{-1} [63] and 2400-2900 cm^{-1} [64] were detected. The species was then employed to probe aurorae on Jupiter [65]. As reviewed by McNab [14] Uranus [66] and Saturn [67] also revealed the presence of H_3^+ in their corresponding atmospheres. Since those pioneering investigations planetary atmospheres still constitute targets for more recent studies [68, 69].

H_3^+ is also a component of the vast clouds of cold dark gas which exist between stars forming the ISM. In fact its abundance in this medium is a key factor which has been subject of discussion [70] as electrons [7] in low density ($n \sim 10^2 \text{ cm}^{-3}$) diffuse clouds can vary the total amount of the ion. Since the first report by Geballe and Oka [71] of detected H_3^+ absorption from measurements of the stellar objects GL2136 and W33A, the ISM has also been the goal of different investigations [72-74]. The spectroscopic study of this species has been employed as a way to explore central regions of the Galaxy [75-77], to analyse cosmic ray ionization rates [78-82] and to investigate star formation regions [83-87].

3.2. The *ortho-para* H_2 conversion

The hydrogen molecule, H_2 , is the dominant species in most of the astrophysical environments and has a major contribution to the physics and chemistry of these media. It also played a fundamental role in the cooling of the gas clouds that gave birth to the very first stars. The molecular hydrogen is constituted of two identical hydrogen

nuclei which are protons of nuclear spin $1/2$, with H_2 in *ortho* (parallel nuclear spins, $I = 1$) and *para* (antiparallel nuclear spins, $I = 0$) forms. An important consequence is that in the ground electronic and the ground vibrational states, the rotational levels of *ortho*- H_2 have odd values of the rotational angular momentum j . On the contrary, the rotational states of *para*- H_2 have even j values. The energy difference between the two lowest rotational levels, $j = 0$ and $j = 1$, is 170 K (0.015 eV). This difference is very important for astrophysics with possible effects the chemistry in the ISM. Thus, some reactions which cannot occur with *para*- H_2 (due for example to an activation energy caused by a potential barrier in the entrance channel) can proceed with *ortho*- H_2 through tunneling effect or because the reaction can become exothermic with the excited molecular hydrogen. A remarkable example is the reaction of N^+ with H_2 , which is the bottleneck in the formation of ammonia. This reaction is endothermic when H_2 is in its ground rotational state because of a barrier close to 170 K which has no influence as soon as the OPR is greater than $\approx 10^{-4}$ [88]. Another example related to the role of deuterium chemistry in prestellar core [87] is the reaction $H_2D^+ + H_2 \rightarrow H_3^+ + HD$, which is endothermic by 232 K if both reactants are in their ground state, but becomes exothermic if both reactants are in their *ortho* state. More generally, the importance of *ortho*- H_2 on the deuteration efficiency of N_2H^+ has been studied in Pagani *et al.* [89, 90].

The initial OPR of H_2 in most of astronomic environments, such as prestellar cores or interstellar dark clouds, is not known. It is generally assumed that newly formed H_2 (on dust grains or in the early universe via the associative detachment between H and H^- and, at high density, the three body recombination $H + H + H$) is initially highly excited. The 4.5 eV energy release of the H_2 formation on grains is indeed large enough to populate many levels of both *ortho* and *para* species. A value of 3, corresponding to the high temperature statistical value, i.e. the ratio of the $2I + 1$ degeneracies of the H_2 nuclear spin states, is thus often assumed. Recent experiments on cold solid surfaces have confirmed this value [91, 92]. Once formed, H_2 in the gas phase tends to relax towards its thermal equilibrium state. However, chemical models have shown that the OPR should not reach its value at thermal equilibrium because the timescale of the *ortho-para* conversion (OPC) process can be significantly longer than the timescale of the thermal evolution (and also than the thermalization time within each modification) e.g. in planetary atmospheres [93], in protostellar shocks [94, 95] or also in the coldest clouds [90, 96]. For the latter case, the OPR is expected to decrease slowly with temperature (from its initial value of 3) but to remain higher than the thermal equilibrium value ($\sim 4 \times 10^{-7}$ at 10 K) [90, 97]. The OPR is therefore expected to depend on the thermal history and lifetime of these astronomical objects. It is thus necessary to model the chemical evolution of the H_2 OPR to understand the evolution of dark clouds. We cannot therefore use the assumption of a thermal equilibrium to estimate the OPR. It is well known today that the OPR of H_2 plays a primordial role in astrophysics, especially for reactions behind the star formation [1, 98, 99]. The OPR ratio is also crucial in the cold (~ 10 K) dark interstellar clouds, where H_2 dominates in abundance, because it determines the excitation of other molecular species [100].

An interesting example is related to the deuterium chemistry where the value of

the OPR influences directly the deuteration. For instance, Pagani *et al.* [89] have shown that the large deuterium enrichment found in some prestellar cores [90] can be explained if the OPR is lower than 0.01. Recent studies show that the *ortho*-H₂ abundance is a key issue to estimate the age of prestellar cores. The chemical models which can help us to discriminate between slow and fast contraction of prestellar cores before they collapse to form protostars relies on the fact that the time for *ortho*-H₂ to disappear is comparable to the dynamical ages we want to measure. Recently, Pagani and co-workers have proposed a chemical clock to measure the age of molecular clouds and prestellar cores [86, 87, 89, 101], based on the deuterium chemistry in the gas phase and for which initial conditions are relatively well known. This approach relies on the long decaying OPR of H₂ (because of the presumably large initial abundance of *ortho*-H₂) and its influence on deuterium enrichment. Indeed, it is directly related to the conversion of H₃⁺ into H₂D⁺ to initiate deuterium enrichment of the molecular gas. The OPR of H₂ plays a crucial role in this model because it controls this conversion [87] and the *ortho-para* H₂D⁺ ratio as first discussed in detail by Pagani *et al.* [102] years ago. More recently, the presence of *ortho*-H₂ has been found to be essential [86, 87] for the spatial dependence of observed deuterated species, such as N₂D⁺ and DCO⁺, in assessing the age of molecular clouds and the time scale of formation of prestellar cores. For instance, the N₂D⁺/N₂H⁺ ratio has been computed along the density profile [101] and it has been found that this ratio increases as the *ortho*-H₂ abundance decreases. Starting at 3, the OPR of H₂ slowly decreases to an almost pure *para*-H₂ form in about a few million years. An upper limit on the age of molecular clouds could therefore be derived by the value of this OPR. The deuterium enrichment of the core takes longer to reach equilibrium and allows to estimate the time necessary to form a dense prestellar core, i.e. the last step before the collapse of the core into a protostar. This study concludes that the fast scenario starting with a high OPR of H₂ is preferred for the L183 case with a dynamical formation which takes less than 1 million years. However, this type of clock is more general and could be applied to other cores to help discriminate between slow and fast contraction theories over a large sample of cases.

As the hydrogen molecule exists under two different forms, *ortho* and *para*, the question is to know how it passes from one state to another, and especially from $j = 1$ to $j = 0$. How does the nuclear spin conversion of H₂ proceed? The answer is not easy but we can attempt to summarise the situation at the present time. In the solid phase, the OPC of H₂ can occur on the surface of magnetic or diamagnetic materials, including amorphous water ice [103] or dust grains [88]. However, the conversion rate on a solid surface is still highly uncertain [91, 104] despite the recent progress done at the experimental level, due the strong dependence on poorly known parameters such as the electronic structure of the surface, the residence time of H₂, the conversion efficiency, etc. [88]. For the nuclear spin conversion of H₂ on solid surface, we refer the reader to the very recent review by Fukutani and Sugimoto [92].

In the gas phase, the simplest OPC process could be radiative. However, radiative transitions for the $j = 1 \rightarrow 0$ transition are very slow with an interconversion lifetime of about 5×10^{20} s, which is greater than the age of the Universe [105].

Pure inelastic (*non reactive*) collisions between H₂ and another species must be

excluded because the nuclear spin state of H_2 cannot change during such processes. Only reactive collisions involving H_2 as a collider and the most abundant hydrogenated species, H , H^+ , H_2 and H_3^+ , as the second collider may lead to the OPC of H_2 . However, due to a large potential barrier of about 5000 K in the entrance channel, the neutral-neutral reaction, $\text{H}_2 + \text{H}$ is not efficient at low temperatures, while it can play a role in warmer regions ($\gtrsim 300$ K) even if the rate coefficient remains relatively small, such as shock-heated gas, photon dominated regions, supernova remnants, and the primordial gas. The other neutral-neutral reaction, $\text{H}_2 + \text{H}_2$, presents an entrance barrier of 60 000 K, and thus its role is totally negligible, except in the planetary atmospheres where the H_2 density is much larger than in the ISM ($\gtrsim 10^{20} \text{ cm}^{-3}$) despite very low rate coefficients [93, 106].

The OPC process in the cold ISM therefore occurs through collisions of molecular hydrogen with protons, H^+ , *i.e.* $\text{ortho-H}_2 + \text{H}^+ \rightarrow \text{para-H}_2 + \text{H}^+$ which is exothermic by 170 K [107, 108]. These collisions are therefore expected to drive the OPR of H_2 in most astrophysical environments, from the primordial to the interstellar gas. It is therefore crucial to know with a high accuracy the cross section and rate coefficient related to this process. Recently, we performed an accurate, fully quantum calculation of the $\text{H}^+ + \text{H}_2$ reaction rate for the *ortho-para* transitions [109–111]. The $j = 1 \rightarrow j' = 0$ conversion seems to be more efficient than the reverse process, with a much higher rate coefficient below 80 K, giving a consistent result with the very low OPR of H_2 at the typical temperature (~ 10 K) found in cold molecular clouds. The new rate coefficient has also a great impact on the deuteration efficiency [101], with an observable like the $\text{NHD}^+/\text{N}_2\text{H}^+$ ratio which is increased by a factor of 10.

In some environments where the H_3^+ relative density is very high, the *ortho-H*₂ + $\text{H}_3^+ \rightarrow \text{para-H}_2 + \text{H}_3^+$ reaction which is also exothermic by 170 K could be the dominant OPC process for H_2 in the gas phase [89, 90]. Unfortunately, an accurate value of the conversion rate is still unknown at the low temperatures of astrophysical interest. Experimental studies are indeed at too high temperature [112] and theoretical studies are only approximate using mainly statistical methods [113–116]. Recent reviews on this reaction gave more details about these different aspects [116, 117].

We also refer the reader to a very recent review on the OPC of H_2 in space written by Lique *et al.* [1] where a detailed overview of the OPC of H_2 in astrophysical media. In particular, the authors discuss the relative role of different OPC processes, such as reactive collisions with hydrogenated species (H , H^+ , H_2 , H_3^+) and interaction with solid surfaces.

4. Association and dissociative recombination

The collision between H^+ and molecular hydrogen is one of the main mechanisms to form H_3^+ . The process requires some energy loss $h\nu$ via a radiative association to stabilize the ion :



mediated by the bimolecular radiative rate coefficient, k_r , or, via a ternary association with the presence of a third colliding object X (for example, another H_2 molecule or

a He atom):



This process is characterized by the ternary rate coefficient k_3 which is usually derived through $k^* = k_r + k_3 [\text{H}_2]$. Early measurements of the apparent binary rate coefficient k^* using drift-tube mass spectrometer apparatus [118, 119] or ring-electrode ion trap techniques [120, 121] led to the calculation of values for k_r and k_3 at temperatures between $T = 80$ and 300 K. Radiofrequency trap experiments with variation of the hydrogen number densities permitted the values of such rate coefficients to be obtained down to 33, 22 and 11 K [121, 122].

The product of the radiative association of Eq. (5), H_3^+ , is in a scattering state and its stability depends on the existence of potential barriers or dynamical restrictions. Those metastable H_3^+ ions may be related to the expected intermediate complexes at the low energy regime of the $\text{H}^+ + \text{H}_2$ collisions [120, 121]. The definition of such an “osculating” complex and the calculation of its lifetime has been connected to different statistical considerations such as the intramolecular energy redistributions required to completely forget the origin after its formation [120, 123, 124].

Interestingly, some deviations from the statistical behaviour have been observed for the stabilization of $\text{H}^+ - \text{H}_2$ complexes at low temperatures. Within a statistical regime k_3 and k_r are expected to display the same dependence with the temperature, but Plašil *et al.* [122] observed that k_3 remains almost constant between 11 and 22 K, but k_r decreases about a ~ 3 factor.

A directly connected process with the presence of H_3^+ in diffuse interstellar clouds is its dissociative recombination (DR) with low-energy electrons:



In fact the observed abundance has been usually viewed as contradicting with the large DR rates measured in laboratory below 1 eV. A possible explanation to give account for the observed discrepancies between the H_3^+ detected in the interstellar medium [71, 72] and the value measured in dense clouds [74] was attempted by means of a model in which clumps of hydrogen responsible for the absorption of infrared radiation are embedded in the medium [125]. Results from storage-ring (SR) experiments [126–128] led to conclude that the process in Eq. (7) occurs too rapidly to explain the amount of the H_3^+ within the stellar medium. Besides the differences with measurements performed with other techniques, such as the flowing-afterglow Langmuir probe (FALP) apparatus [129, 130], those experimental DR rates differ orders of magnitude with respect to theoretical estimates [131].

A complete understanding of the dynamics behind the observed DR rates took some years of investigations [132, 133]. Kokoouline *et al.* [134] proposed a method including the Jahn-Teller distortion of the H_3^+ ion due to the effect of the incoming low-energy electron, which gave some insight of the FALP cross sections. Indications of the contribution from both rotational excitations [126, 135] and the nuclear spin of the ion [136] led to subsequent improvements in the theoretical approaches as the fully

quantal description by Kokoouline and Greene [137, 138] which takes into account all internal degrees of freedom of the ion. Later work indicated that discrepancies about the precise rotational temperature at which the ions remain stored in SR rate measurements could be the origin of the differences between theory and experiment regarding the collision-energy and rotational-dependence of the DR rate coefficients [139–141]. Current progress is now focused to control the rotational state distribution of the ions in the SR apparatus [141, 142].

An extra ingredient under consideration in the study of DR of H_3^+ regards the *ortho-para* character of the ion. Differences on the recombination rate coefficients for H_3^+ formed from either *ortho*- H_2 or *para*- H_2 and the possible implications within an astrophysical context [143] have been the subject of numerous studies. Despite theoretical calculations predicted a faster recombination for the ground-state *ortho*- H_3^+ at low collision energies [138], further investigations suggested a higher DR rate for *para*- H_3^+ than for *ortho*- H_3^+ [136, 139, 143]. The nearly two times difference between both rates found by Tom *et al.* [143] was nevertheless estimated as too modest for an astrophysical scale to play a determinant role on the OPR of the ionic species in the diffuse interstellar medium. Near infrared cavity ring down spectrometer measurements with electrons at 77 K of the effective recombination rate coefficients [144, 145] found that the ratio between the *para* and *ortho*- H_3^+ cases increases when a higher population of relative *para*- H_2 is employed in the experiments. The evolution of the H_3^+ ion was monitored *in situ* during the afterglow as a function of spin, rotational excitation and temperature.

5. The dynamics of the $\text{H}^+ + \text{H}_2$ reaction

5.1. Experimental work

One of the earliest reports on elastic scattering measurements of H^+ and H_3^+ in molecular hydrogen comes from the work by Simons *et al.* [146]. Ions from a water-cooled arc were directed as a collimated beam into a chamber with the molecular gas [147]. After the collision between ions and H_2 “unscattered” and “scattered” portions are collected separately by means of a small decelerating potential to draw slow moving ions. The measurement of the resulting current allows to observe the neutralization and inelastic scattering processes. This technique was employed to measure initial kinetic energy of the ion and $\text{H}^+ + \text{H}_2$ cross sections in the velocity range of 2 to 135 volts. The authors evaluated potential laws, $V = -Kr^{-n}$, for the interaction between the ion and the gas molecule by examination of the angular change in the $\text{H}^+ - \text{H}_2$ direction of the ion after its interaction with H_2 . The final expression was found to depend on the velocity of the ion. This information was used afterwards in early studies of the mobility of hydrogen ions in molecular hydrogen [148].

Refinements of the original apparatus led to more precise measurements of both elastic and inelastic cross sections for low energy D^+ ions in deuterium gas between 4 and 400 eV [149]. The comparison with the previously reported results for $\text{H}^+ + \text{H}_2$ revealed that charge exchange cross sections for the deuterated case were smaller.

Velocity and angular spectra of reaction products and angular displacement be-

tween reactants and products were obtained for charge (and no charge) transfer reactions $D^+ + HD$, $D^+ + D_2$ and $H^+ + D_2$ [150] by means of a cross-beam apparatus [151]. Only products along a narrow cone about the forward direction were detected and therefore no accurate measurements of the total cross section were made. The authors interpreted that a variety of possible dynamical mechanisms were compatible with the obtained spectra. In particular they attributed peaks observed near the center of mass (CM) to the formation of a persistent intermediate complex. This was the main route for the channels which lead to D_2^+ formation and was also found to be a significant contribution for the formation of HD^+ , a process for which the role played by direct mechanisms was also apparent. H_2^+ was also detected as a product in the collision of H^+ ions with molecular hydrogen at high energies (≥ 70 eV) in the experimental investigation performed by Koopman [152].

A modified version of the same molecular beam apparatus employed in Ref. [150] was used to obtain absolute cross sections, product translational energy distributions (TEDs) and product velocity contour diagrams for the $D^+ + HD$ and $H^+ + D_2$ reactions [153]. The comparison with trajectory surface hopping (TSH) calculations revealed that the dynamics of the reactive processes can shift from a short-lived collision complex mediated pathway for energies below 3 eV to direct impulsive mechanisms.

H^+ ions produced by bombarding NH_3 with electrons were passed to a reaction chamber to collide with D_2 in the experiment performed by Maier [154]. Primary and secondary ions D_2^+ , HD^+ and D^+ were detected by means of a mass spectrometer as outputs of the corresponding charge transfer, atom transfer and substitution reactions. Cross sections for initial kinetic energies in the CM between 0.3 and 80 eV were measured. Thresholds for the $H^+ + D_2 \rightarrow D_2^+ + H$ and $H^+ + D_2 \rightarrow HD^+ + D$ reactions were observed whereas the cross section for the $D^+ + HD$ product channel was found to decrease rapidly as the energy increases. In fact, for high energies, $E_{CM} > 8$ eV, D^+ was mainly produced after the total dissociation $H^+ + D_2 \rightarrow D^+ + D + H$.

New measurements of the integral cross sections (ICSs) for the $H^+ + D_2$ reaction were performed with a guide beam technique in which a tandem mass spectrometer with inhomogeneous oscillatory electric fields guides the primary ions through a scattering chamber [155]. The experiment was not capable to distinguish whether the D^+ ions came from the $D^+ + HD$ product channel or whether were originated after the total $D^+ + H + D$ fragmentation. Agreement was found with measurements by Maier [154] and TSH calculations by Krenos *et al.* [153] at 4, 5.5 and 7 eV collision energies, but some discrepancies were observed with respect to results reported in other experimental works [150, 153, 156].

Subsequent investigations started to focus on the measurement of rate coefficients. The study by Henchman *et al.* [157] employed a temperature variable selected ion flow tube (SIFT) in which H^+ and D^+ were introduced in a He chamber by injection of H_3^+/D_3^+ at large relative energies (> 10 eV) to ensure complete collisional dissociation. Rate coefficients were measured for the $H^+ + D_2 \rightarrow HD + D^+$, $H^+ + HD \rightarrow H_2 + D^+$ and the corresponding reverse reactions between 200 and 300 K. One of the possibilities to explain the decreasing behaviour as the temperature raises observed for the exoergic processes, those initiated from $D^+ + HD/H_2$, relies on the possible formation of a sufficiently long-lived intermediate complex before the onset of the products.

Both the lifetime of such a complex and the rate for its formation reduce with increasing temperature, which would also explain the decrease of the overall reaction rate constant.

The drift apparatus employed by Villinger *et al.* [158] for their investigation of the $\text{H}^+ + \text{D}_2$ and $\text{D}^+ + \text{H}_2$ reactions consisted on a helium chamber in which H^+ and D^+ ions were conducted under the influence of an electric field to an analyzing system located at the end of the drift tube. Rate coefficients are obtained via the reduction of the detected primary ion signal after the reactant gas (D_2 and H_2) is introduced in the chamber. The smooth extrapolation observed at the low temperature range under study with respect to results reported by the SIFT experiment of Ref. [157] for the $\text{H}^+ + \text{D}_2$ case revealed a possible statistical behaviour of the process. Some disagreement between the SIFT measurement at 295 K ($1.7 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and the drift result at 0.043 eV ($1.1 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) suggested on the contrary the failure of the Langevin requirements for the $\text{D}^+ + \text{H}_2$ reaction.

Most of the activity in this direction was reviewed in the comparisons performed by Gerlich in different studies [159, 160]. For the $\text{H}^+ + \text{D}_2$ reaction, the rate coefficients in terms of the collision energy exhibit an almost constant behaviour as the energy decreases below $E_c \sim 0.1$ eV. This Langevin type trend, found for merged beam results and which can be reproduced by statistical approaches down to the 10^{-2} eV energy range [159], differs nevertheless with some of the other experimental results. Thus the guide ion beam (GIB) apparatus of Ochs and Teloy [155] recorded a too steeply increase as the energy falls; the drift tube investigation by Villinger *et al.* [158] reported too small rate coefficients and the variable-temperature selected ion measurements by Henchman *et al.* [157] showed a different trend. The only experimental results with qualitatively similar energy dependence were those from an improved GIB study [159] with respect to that performed in Ref. [155]. These rate coefficients display a maximum at ~ 300 meV and fall slowly below $1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at a collision energy of 25 meV.

A somehow better agreement was found for the $\text{H}^+ + \text{D}_2$ reaction. The comparison shown in Ref. [159] revealed that the energy dependence of the effective rate coefficient observed in the beam study by Ochs and Teloy [155] and the drift measurements by Villinger *et al.* [158] displayed a maximum about 0.3 eV translational energy.

Laboratory energy distributions of D^+ ions produced in the $\text{H}^+ + \text{D}_2$ reaction have been measured by Gerlich [159, 161]. In particular, in Ref. [161], distributions for different laboratory angles at energies between 0.4 and 2 eV were presented in comparison with QM, quasi-classical trajectory (QCT) and statistical calculations.

The nonreactive inelastic collisions for the H_3^+ system have also been the subject of extensive study over the years. In this process, the collision of the ion leads either simply to its rovibrational excitation, or to the transfer of the charge to the diatom. Moore and Doering [162] reported one of the first experiments designed to measure the energy loss of inelastically scattered ions without charge transfer from H_2 . In spite of not all vibrational peaks were completely resolved, pure vibrational transitions $\text{H}^+ + \text{H}_2(v=0) \rightarrow \text{H}^+ + \text{H}_2(v'=1-3)$ and those for D_2 were observed between 100 and 600 eV. Angular distributions and their energy dependence were investigated by means of the energy-loss technique. The importance of the measured cross sections

suggested the role played by vibrational excitation in proton-gas interactions. The vibrational excitation of H_2 after the impact with H^+ and D^+ was also investigated for laboratory energies between 100 and 1500 eV [163]. For lower energies, cross sections were obtained for forward-scattered protons ($\theta = 0^\circ$ to $\theta = 1.9^\circ$). The possible competition between elastic scattering and charge-transfer processes was analysed in terms of the energy range.

The first state-to-state differential scattering experiment for the charge-transfer process $\text{H}^+ + \text{H}_2(v = 0) \rightarrow \text{H} + \text{H}_2^+(v')$ was reported in the time-of-flight (TOF) spectroscopy investigation by Niedner *et al.* [164]. Energy loss, TOF and laboratory angle distributions were measured at $E_{\text{lab}} = 20$ eV. The comparison between the inelastic (production of $\text{H}^+ + \text{H}_2(v')$) and elastic processes provided evidences of a two-step charge transfer mechanism in which sufficiently high vibrational excitation of $\text{H}_2(v' \geq 4)$ on the lower reactant surface could be followed by the charge-transfer pathway.

In fact, it was the significant contribution to the total scattered intensity coming from inelastic events which encouraged authors of Ref. [165] to perform the full resolved investigation of vibrational-state-selected differential cross sections (DCSs). Angular cross sections keeping either the energy or the CM polar angle fixed were reported [165, 166] for a CM energy range between 4 and 21 eV. Rotational excitations, lower in intensity than the vibrational excitations, were also resolved in further crossed beam experiments [167, 168].

One of the breakthroughs in the understanding of the dynamics behind the H_3^+ reaction came with the experiments performed with the Rydberg H atom TOF technique [169]. In principle it is possible to assume an effective equivalence between the dynamics of the ion-molecule process $\text{H}^+ + \text{D}_2 \rightarrow \text{HD} + \text{D}^+$ and that responsible of the collision between an hydrogen atom in a highly excited Rydberg state, $\text{H}^*(n)$, with $n \sim 45 - 50$, and the deuterium molecule, $\text{H}^*(n) + \text{D}_2 \rightarrow \text{HD} + \text{D}^*(n)$. The electron in the H atom would be then behaving as a spectator and the collision is in fact occurring with H acting in essence as an ion. Rotationally resolved product distributions for the Rydberg-atom reaction were found to agree with those obtained at a single scattering angle for the proper ion-atom reactive collision at a collision energy of 0.524 eV [170, 171].

This experimental technique has been successfully employed to probe the dynamics of the $\text{H}^+ + \text{D}_2$ reaction. Besides TOF spectrum of the scattering products and TEDs at different laboratory angles [170], total and state-to-state DCSs and product rotational distributions at $E_c = 0.524$ eV have been reported [171]. In a different experiment performed for the same reaction at $E_c = 530$ meV collision energy with the same technique, measured rotational populations of HD were obtained [172]. The comparison with prior distribution theory revealed that those product states were statistically populated. Measured kinetic energy spectra (KES) for different laboratory angles, $\Theta_{\text{lab}} = 9^\circ, 17^\circ, 24^\circ, 32^\circ, 42^\circ$ and 52° were compared with theoretical simulations from DCSs obtained from QM, QCT and statistical approaches [173].

By means of recent refinements in the experimental Rydberg H-atom TOF set up, with a modified design which reduces the attenuation of the scattered Rydberg H-atom beam, it has been now possible to measure full quantum-state resolved DCSs

for the $H^*(n = 46) + o\text{-D}_2 \rightarrow \text{HD} + D^*(n')$ reaction [174]. The new experimental results at $E_c = 0.526$ eV cover a much more extended angular range than the originally reported DCSs [170, 171] and show a marked preference for the forward scattering direction (about 2.3 times larger than the corresponding value through $\theta \sim 180^\circ$), as opposed as the observed forward-backward symmetry of the $H^+ + \text{D}_2$ reaction. This result would then question the apparent equivalence previously established between the Rydberg H-atom process and the ion-diatom collision. As suggested by Hayes and Skodje [175] this could be explained by a significant effect of the H atom with the electron excited in a high Rydberg state on the reaction altering the angular distribution. However, the corresponding rotational distributions for both processes showed a reasonably good agreement, which would invite again to think that the H^+ ion behaviour could be assumed as that expected from a H atom with an electron in a Rydberg state. In order to complicate things, the rotational distributions for a slightly lower energy $E_c = 0.5$ eV, exhibited a saw-toothed profile [176].

5.2. Theoretical studies

The early investigations on the mobility of H^+ ions in H_2 [146, 148] constituted the first step beyond the QM calculations to obtain the interaction energy between the ion and molecular hydrogen performed time before. Those calculations of the elastic cross sections employed exponential law expressions as commented before in Section 5.1 and Morse functions to describe the $H^+ - H_2$ interaction averaged over all orientations.

The first dynamical calculation using an *ab initio* PES on the H_3^+ reaction was performed by Csizmadia *et al.* [177]. The study employed a potential curve composed of three superimposed Morse-like functions which were rotated for different interparticle distances to produce a PES for a given $(H-H-H)^+$ angle. Authors performed a classical trajectory calculation for the $D^+ + H_2$ reaction on that surface, finding the formation of an intermediate complex with typical lifetimes of about 10^{-13} s. The almost forward-backward symmetry of the DCS at 4.5 eV, with a purely statistical profile, supported this possibility. Wolfgang [178] also suggested in his study of chemical reactions a transition from a persistent complex to a direct mechanism for $D^+ + H_2$ as the energy changes a few eV.

These conclusions however were obtained without any consideration of possible non-adiabatic charge-transfer processes. H_3^+ was soon employed as a prototype system suitable for testing extension of the classical trajectory approach which accounts for transitions to different PESs. The TSH method proposed by Tully and Preston [179, 180] in which nuclei are assumed to move classically on a single PES until either an avoided surface crossing or a region with noticeable nonadiabatic coupling is reached, was used to calculate cross sections for the $H^+ + \text{D}_2$ reaction. PESs for the two lowest singlet states of H_3^+ were obtained by means of the diatomics-in-molecule procedure and the comparison of the values for the three possible product channels, $D^+ + \text{HD}$, $D + \text{HD}^+$ and $H + \text{D}_2^+$, with experimental results [154, 156] revealed a fairly good agreement. Subsequent investigations for the $H^+ + \text{D}_2$ and $D^+ + \text{HD}$ reported the comparison of calculated velocity distributions, cross sections and product state

distributions with molecular beam measurements [153] for a relative energy range covering 1 and 7 eV. Below 3 eV the reactions were found to involve a short-lived collision intermediate species whereas the main dynamical mechanism is a direct impulsive process for energies larger than 4 eV.

A similar energy range was covered in the TSH study performed by Ichihara *et al.* [181] of the $D^+ + H_2$, $D^+ + D_2$ and $H^+ + D_2$ reactions. The authors compared their calculated cross sections for the formation of H^+ / HD^+ , D_2^+ and $D^+ / D_2^+ / HD^+$ respectively with previous experimental results [155, 182]. Discrepancies between both sets of data were attributed to the necessity of a more extended version of the TSH approach, as that proposed later by Zhu *et al.* [183, 184] and Li and Han [185].

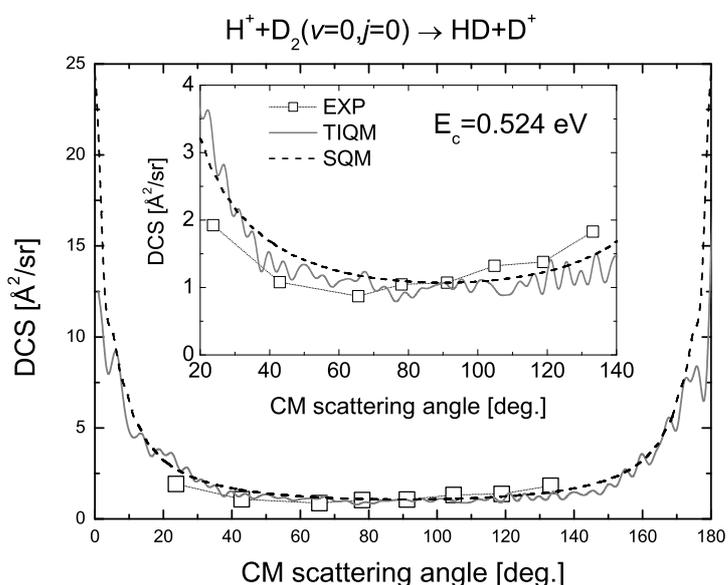


Figure 1. Differential cross section of the $H^+ + D_2 \rightarrow D^+ + HD$ reaction at $E_c = 0.524$ eV. Comparison of experimental result by Song *et al.* [171] (squares and dotted line) and the TIQM (grey solid line) and SQM (black dashed line) distributions from Ref. [173].

Vibrational inelastic $H^+ + H_2(v) \rightarrow H^+ + H_2(v')$ and vibrational charge transfer $H^+ + H_2(v) \rightarrow H + H_2^+(v')$ processes have been also studied [186–189] by means of QM approaches such as the vibrational close-coupling rotational infinite-order-approximation originally applied by Schinke and McGuire for the H_3^+ system [190]. It was then possible to establish the comparison with previously measured ICSs, DCSs and transition probabilities [167, 191, 192]. Hyperspherical coordinates investigations were reported under restrictions such as collinear geometries [193] and zero total angular momentum [3]. The time dependent wave packet (TDWP) calculation by Marković and Billing was also restricted to $J = 0$ [194]. In their study, which

included a comparison with TSH results, cross sections for the formation of an intermediate complex decreased rapidly as the collision energy increases. Above 4.5 eV, the dissociation limit of H_2 and D_2 in the ground vibrational state, no long-lived trajectories were found. The full three dimensional treatment of the corresponding nonadiabatic effects was nevertheless performed some time afterwards by means of exact TDWP approaches for the $\text{H}^+ + \text{D}_2$ and $\text{D}^+ + \text{H}_2$ reactions at sufficiently high energy regimes (1.7–2.5 eV) to appreciate the competition between the different dynamical reaction pathways [195–197]. Works by Ochs *et al.* [155], Niedner *et al.* [164] and Schlier *et al.* [182] provided the experimental benchmark for cross sections of these processes.

The possible complex-forming character of the process on the ground state electronic surface before the onset of both reactive and non-reactive charge transfer channels has been investigated in detail by means of the statistical quantum method (SQM) of references [198, 199]. An early review of studies in the present reaction and some other atom-diatom processes in which an insertion mechanism may also play a role can be found in Ref. [200]. The experimental DCSs obtained for $\text{H}^+ + \text{D}_2$ at $E_c = 0.524$ eV by Song *et al.* [171] were reproduced by statistical means [173, 201]. Despite the comparison was not possible at the forward and backward scattering directions, since the experimental results were restricted to the $20^\circ \leq \theta \leq 140^\circ$ angular range, the good agreement found between the statistical predictions and the measured DCS supported the already reported suggestion of a complex-forming mechanism for the reaction at such energy [171, 172]. Fig. 1 shows the corresponding comparison between the experimental angular distributions and those obtained by means of the above mentioned SQM approach and a time independent QM (TIQM) calculation. The statistical predictions were found to overestimate the values at $\theta \sim 0^\circ$ and $\theta \sim 180^\circ$, a feature which nevertheless, seems to be corrected with slight variations of the value of E_c under consideration [173, 202].

The importance of the role played by complex-forming pathways on the overall H_3^+ dynamics at this intermediate energy range ($0.1 \text{ eV} \leq E_c \leq 0.6 \text{ eV}$) is further confirmed by the good accord observed between simulated KES recorded in the experiment by Wrede *et al.* [172] and both TIQM and SQM results [173]. Examples of such a comparison at $\Theta_{\text{lab}} = 9^\circ$ and 24° are shown in Fig. 2. As revealed in Ref. [173], although sideways scattering ($\Theta_{\text{lab}} = 52^\circ$) is better simulated than backward scattering ($\Theta_{\text{lab}} = 9^\circ$) and there is significant contribution from inelastic processes in the experiment, both theoretical approaches give account for most of the features exhibited by the measured spectra. In particular the slight deviations observed between the SQM and TIQM DCSs, employed to obtain the KES spectra, did not affect to the good performance of the statistical technique.

Besides the reported apparent change in the dynamics of the process as the energy increases well above the onset of charge-transfer channels, deviations from a statistical behaviour were also found at much lower energies for the title reaction and its isotopic variants [161, 203–205]. Thus for example cumulative reaction probabilities obtained by means of a QCT version of the SQM approach (SQCT) [206, 207] start to overestimate both purely QCT and QM results for the $\text{H}^+ + \text{D}_2$ reaction [203] above $E_c \sim 0.6$ eV. Statistical cross sections for the same reaction were found to be larger

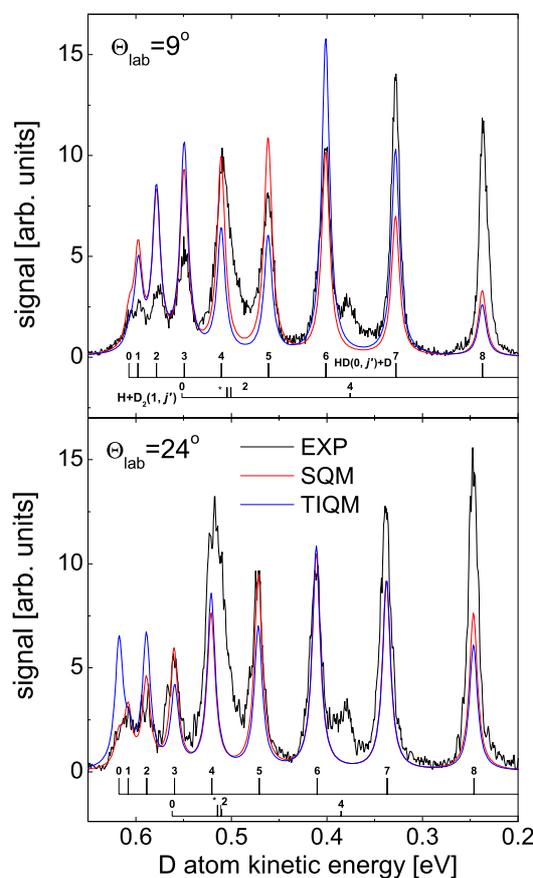


Figure 2. Kinetic energy spectra for the $\text{H}^+ + \text{D}_2 \rightarrow \text{D}^+ + \text{HD}$ reaction at $E_c = 0.524$ eV at two values of the laboratory angle, $\Theta_{\text{lab}} = 9^\circ$ and 24° , measured by Wrede *et al.* [172] in black line. Theoretical simulations correspond to the time independent QM (red line) and SQM (blue line) calculations of Ref. [173].

than those calculated with a TDWP in Ref. [204] and SQCT $P(J)$ values are clearly above the QM probabilities at $E_c = 1.2$ eV. Mean potential statistical theory results on the same reaction [208] yielded cross sections which slightly improved the comparison with the QM values. A similar investigation on the $\text{D}^+ + \text{H}_2$ reaction however concluded that the process could be deemed to be more statistical than $\text{H}^+ + \text{D}_2$ [205]. The direct comparison with the experiment revealed that the SQCT method yielded simulated KES cooler than the measured ones and rate coefficients in terms of the energy which do not reproduce the trend of the measurements as the energy increases above $E_c \sim 0.2$ eV [161].

At a low energy range ($E_c \lesssim 0.1$ eV), the average trend followed by the TIQM cross sections for the $\text{H}^+ + \text{H}_2$ reaction is fairly well reproduced by statistical means [109, 209]. Examples for the $j = 0 \rightarrow j' = 1$ and $j = 1 \rightarrow j' = 0$ cases are shown

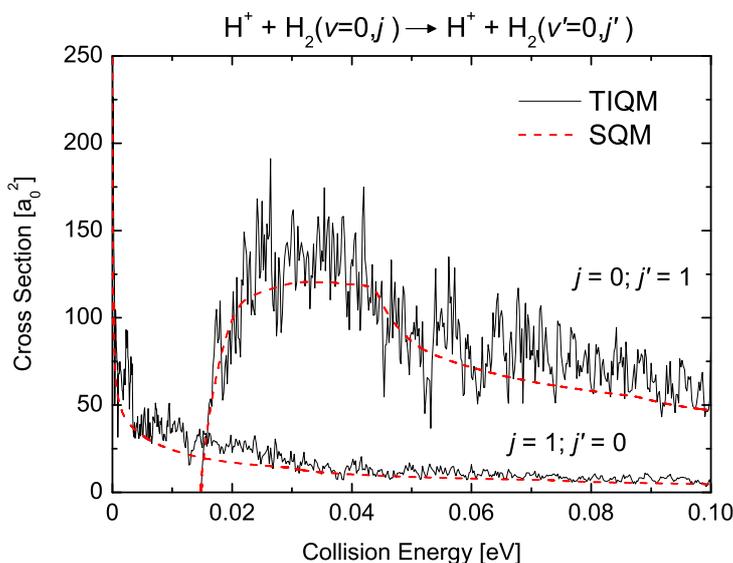


Figure 3. Cross sections for $\text{H}^+ + \text{H}_2(v=0, j) \rightarrow \text{H}^+ + \text{H}_2(v'=0, j')$. TIQM (black solid line) and SQM (red dashed line) results from Ref. [109] are compared at the $E_c < 0.1$ eV range for the $j=0 \rightarrow j'=1$ and $j=1 \rightarrow j'=0$ cases.

in Fig. 3. The TIQM results exhibit a pronounced resonance structure which has been suggested to be responsible for radiative association [121] and which can not be reproduced by the SQM calculation. However the statistical predictions clearly give account for the overall behaviour in terms of the energy of the QM cross sections.

Despite the noticeable discrepancies between the QM and statistical DCSs at even smaller energies ($E_c \sim 10^{-6}$ eV) observed for the proton transfer H_2 OPC reactions [110], the investigation of the rate coefficient $k(E_c)$ down to 10^{-3} eV revealed evident signals of a statistical behaviour for the $\text{D}^+ + \text{H}_2$ process at such low energy regime [210]. As shown in Fig. 4, the almost constant behaviour of the experimental coefficients [159] is well reproduced by both the SQM and TIQM calculations [210], thus suggesting the major role played by complex-forming mechanisms. The same assumption is the basis for the calculation of the rate coefficient for the reaction by means of a statistical mixing model [211]. This feature differs however from the deviations observed between SQCT rate coefficients and those obtained by means of a purely QCT estimation for the same reaction as the energy increases beyond $E_c \sim 0.3$ eV [161].

5.3. Numerical difficulties

Numerical approximations such as the centrifugal sudden (CS) approach have been found to introduce noticeable deficiencies in calculations on the $\text{D}^+ + \text{H}_2$ and $\text{H}^+ + \text{D}_2$ reactions [195, 201]. The nonadiabatic TDWP investigation by Chu and Han [195]

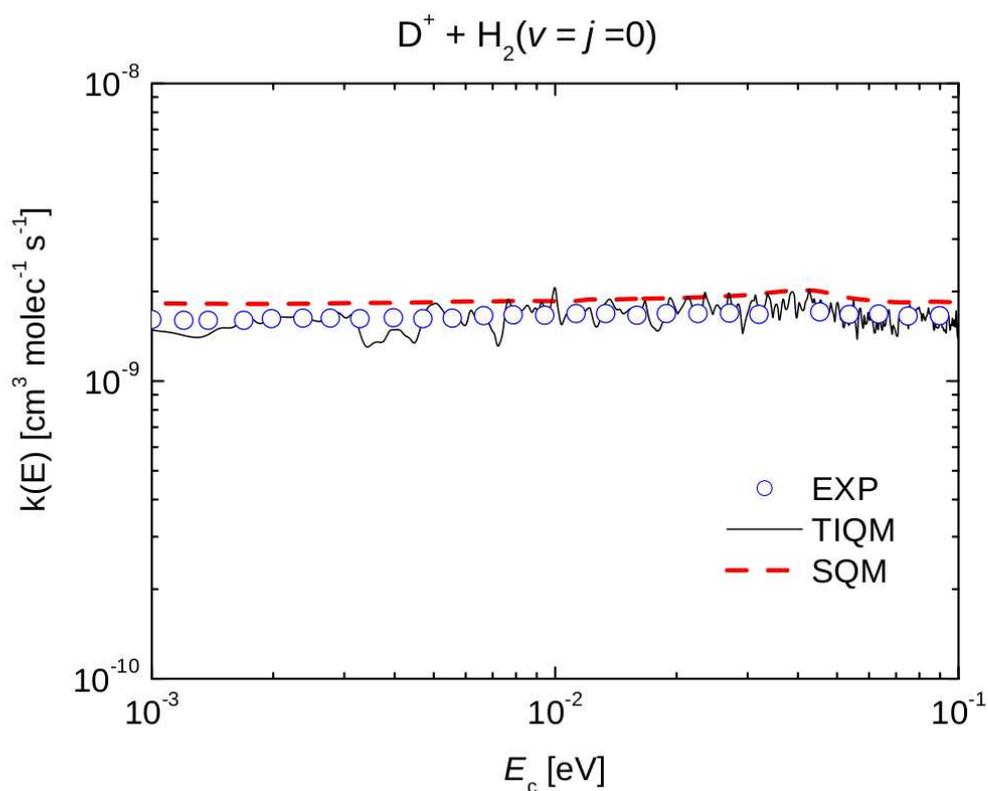


Figure 4. Rate coefficient in terms of the collision energy for the $D^+ + H_2 \rightarrow H^+ + HD$ reaction. TIQM (black solid line) and SQM (red dashed line) results from Ref. [210, 212] are compared with the experimental (empty circles) results by Gerlich [159].

revealed significant differences between the coupled-channel (CC) probabilities for total angular momentum $J \leq 25$ and those obtained under the CS approximation specially for the $D^+ + H_2 \rightarrow D + H_2^+$ and $D^+ + H_2 \rightarrow H^+ + HD$ channels. Evidences of failures in the CS calculations extended for the three possible product channels (the reactive charge transfer pathway included) when the corresponding ICSs were compared. Restricted to the reactive non-charge transfer process, authors of Ref. [201] tested different possibilities for Coriolis decoupling within a wave packet method in order to calculate ICSs. Besides the usual CS approach, a statistically modified CS (SMCS) and an adiabatic CS (ACS) variants were attempted to investigate the $H^+ + D_2 \rightarrow D^+ + HD$ reaction. In the SMCS formalism centrifugal barriers were minimized assuming the maximum possible value of the projection Ω of both the total angular momentum J and the diatom rotational number j . Within the ACS proposal, the effective centrifugal term was built with the lowest eigenvalue of the matrix for the rotational terms formed with all possible values of Ω . Although the SMCS approach was found to improve the comparison with the CC ICSs with respect to the ACS case, a full agreement was not achieved. On previous studies similar Coriolis decoupling schemes, such as retaining exclusively the $\Omega = J$ contribution, were also proved wrong for the $D^+ + H_2$ reaction [213].

Similar indications of the failure of the CS approximation for the title reaction were evident in the comparison performed between the predictions of the SQM approach and from the SQCT version for the $\text{H}^+ + \text{H}_2$ and $\text{H}^+ + \text{D}_2$ reactions [206, 207]. The main differences observed in state-to-state reaction probabilities in terms of the total angular momentum at specific values of the collision energy, $P_J(E_c)$, and the corresponding rovibrational distributions were purely due to the use of the CS approach in the SQM calculation. Once the CC version is employed the discrepancies between both statistical results at large values of J in the reaction probabilities and on the population of some $\text{H}_2(v', j')$ and $\text{HD}(v', j')$ product states are solved.

Interestingly the QCT method was found to have some difficulties to give account of some of the main dynamical features of the H_3^+ reaction. On one hand the $P_J(E_c)$ probabilities revealed a noticeable underestimation of the QM results as predicted by means of the trajectory approach for both the $\text{H}^+ + \text{H}_2$ [202] and $\text{H}^+ + \text{D}_2$ [173] reactions. QCT rotational populations were also abnormally below results from QM and statistical calculations. Given that a large number of trajectories get trapped at the potential well region for a considerably long time ($\tau \sim 500$ fs) at large values of J , the only explanation for such a behaviour has to rely in the fact that the intermediate complex formed contains enough rotational energy to fragment back to reactants [173]. The issue was investigated in subsequent studies in which Gaussian and histogram binning within the QCT framework were comparatively tested [204, 205]. Bonnet proposed an adiabatical correction to the Gaussian weighted trajectory approach to improve the comparison of opacity functions, $P(J)$, with TIQM results for the $\text{H}^+ + \text{H}_2$ and the $\text{H}^+ + \text{D}_2$ reactions [214].

In addition to this, QCT DCSs do not exhibit the maximum peaks at both the forward and backward scattering directions obtained at some energies in the QM results. The lack of this characteristic signal of a complex-forming dynamics of the reaction responds to the neglect of the parity conservation in classical mechanics [215]. The above mentioned SQCT was designed to avoid this problem [206] and has been applied successfully to reproduce angular distributions on different isotopic variants of the H_3^+ reaction [204, 206, 207].

QM techniques also present numerical difficulties for the present reaction. Thus the number of helicity components Ω employed has been also found to be a sensitive parameter to take into account. The differences observed between the results obtained by means of a TDWP approach and statistical predictions were originally attributed to possible deviations from a complex-forming mechanism for the $\text{H}^+ + \text{D}_2$ and $\text{D}^+ + \text{H}_2$ reactions [201]. However as reported later [202] the maximum value $\Omega_{max} = 10$ considered in the wave packet calculation might have not been enough for $J > 20$ at collision energies such as $E_c \sim 0.44$ eV. Analogously the precise value of the asymptotic region considered in TIQM calculations can be an issue. Propagation up to an asymptotic matching distance of $\rho_{max} = 30$ a_0 yielded rate coefficients with an anomalous behaviour as the collision energy decreased below 10^{-2} eV [216]. Numerical tests performed increasing the maximum distance R_{max} of the similar propagation required in the SQM approach [210] revealed that ρ_{max} has to be enlarged to ensure the correct tendency of the rate coefficient [212].

One of the distinct features of the H_3^+ dynamics is the highly oscillatory behaviour

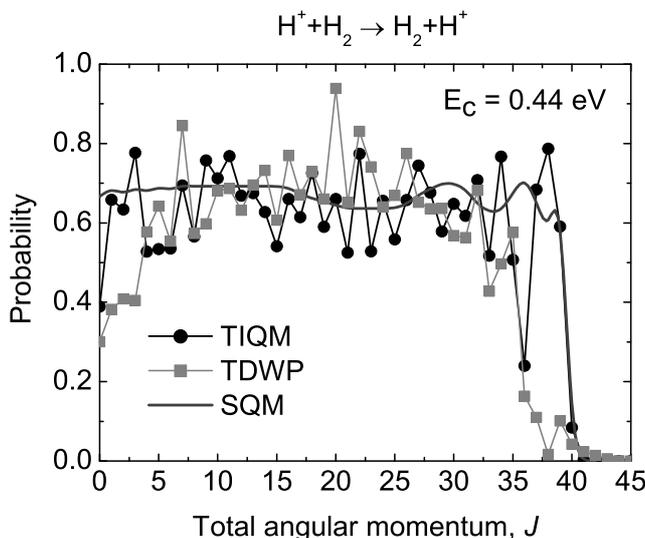


Figure 5. Reaction probability in terms of the total angular momentum J for the $\text{H}^+ + \text{H}_2 \rightarrow \text{H}_2 + \text{H}^+$ at $E_c = 0.44$ eV obtained by a TDWP (grey solid circles), TIQM (black solid circles) and SQM (black solid line) methods [202].

of the corresponding reaction probabilities. This effect can be observed both in terms of the energy and of the total angular momentum. The presence of extremely narrow resonances preclude for instance the perfect agreement between TIQM and TDWP calculations [173, 202, 217]. An example of these oscillations as a function of J is shown in Fig. 5 where opacity functions, $P(J)$, at $E_c = 0.44$ eV for the $\text{H}^+ + \text{H}_2$ reaction obtained by different methods are displayed [202]. In particular the complex-forming nature of the process at that energy is suggested by the agreement observed between the overall trend of both the TDWP and TIQM probabilities with the statistical predictions.

Cross sections also exhibit large fluctuations over narrow energy ranges, as shown before in Fig. 3 for the case of the H_2 OPC in $\text{H}^+ + \text{H}_2$ reactions. The partial waves average required to calculate ICSs seems to be not sufficient to wash out the highly structured profile of the corresponding reaction probabilities. Analogously, the strong variation with energy of state-resolved DCS made authors of Ref. [161] to carry out the corresponding average over collision energies in the theoretical simulations of experimental results to take into account the possible changes of the state resolved flux into the specific range of scattering angles sampled by the measurements.

6. Acknowledgements

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