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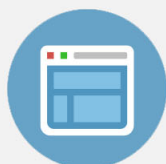
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Dynamics of the $D^+ + H_2 \rightarrow HD + H^+$ reaction at the low energy regime by means of a statistical quantum method

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The $D^+ + H_2(v = 0, j = 0, 1) \rightarrow HD + H^+$ reaction has been investigated at the low energy regime by means of a statistical quantum mechanical (SQM) method. Reaction probabilities and integral cross sections (ICSs) between a collisional energy of 10^{-4} eV and 0.1 eV have been calculated and compared with previously reported results of a time independent quantum mechanical (TIQM) approach. The TIQM results exhibit a dense profile with numerous narrow resonances down to $E_c \sim 10^{-2}$ eV and for the case of $H_2(v = 0, j = 0)$ a prominent peak is found at $\sim 2.5 \times 10^{-4}$ eV. The analysis at the state-to-state level reveals that this feature is originated in those processes which yield the formation of rotationally excited $HD(v' = 0, j' > 0)$. The statistical predictions reproduce reasonably well the overall behaviour of the TIQM ICSs at the larger energy range ($E_c \geq 10^{-3}$ eV). Thermal rate constants are in qualitative agreement for the whole range of temperatures investigated in this work, 10–100 K, although the SQM values remain above the TIQM results for both initial H_2 rotational states, $j = 0$ and 1. The enlargement of the asymptotic region for the statistical approach is crucial for a proper description at low energies. In particular, we find that the SQM method leads to rate coefficients in terms of the energy in perfect agreement with previously reported measurements if the maximum distance at which the calculation is performed increases noticeably with respect to the value employed to reproduce the TIQM results. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4816638>]

I. INTRODUCTION

Due to its abundance in the universe and the important role played in an astrophysical context, H_3^+ has been the subject of a large number of both experimental and theoretical studies in the last years. As detailed for instance in successive reviews by Oka,^{1,2} the infrared spectroscopy of the “simplest stable polyatomic system,” has constituted itself, a separate chapter in chemistry. The analysis of the emission bands from interstellar clouds and planets from our solar system has revealed the active presence of such a molecular species. Besides the interest to reproduce the bound states of the molecule with a sufficiently high precision to calculate the rovibrational spectra, the corresponding scattering dynamics related with the system constitutes a crucial issue to understand the ortho-para conversion of molecular hydrogen. Collisions of H_2 with H^+ (or alternatively with H_3^{+3} depending on the environment³) seem to drive the transition between odd and even states of the molecular hydrogen rotational parity. Thermal rate constants for this ortho-para conversion^{4,5} are thus employed as necessary input in astrophysical models to design chemical clocks to measure the age of molecular clouds and prestellar cores.^{6,7}

Several potential energy surfaces (PES) are nowadays available at the literature for the H_3^+ system.^{8–13} The dis-

tinct topology of these surfaces has been found to introduce some subtle effects on the dynamics of the corresponding reactive scattering processes. In particular, PESs from Refs. 9 and 10 were comparatively tested¹⁴ for the $H^+ + D_2 \rightarrow HD + D^+$ reaction. Reaction probabilities, rovibrational distributions, and differential cross sections (DCSs) at collision energies of $E_c = 0.1$ eV and 0.524 eV obtained for each surface revealed differences which seem to be more noticeable as the energy decreases. It is precisely at the low energy regime where the necessity of an accurate description of the PES to give account for the dynamics of the reaction becomes specially demanding. In this paper, we have used the surface developed by Velilla *et al.*¹² which treats long range electrostatic interactions analytically.

Some of the earliest experimental work on the exchange $D^+ + H_2 \rightarrow H^+ + HD$ reaction has been devoted to measure rate constants.^{15–19} Holliday *et al.*²⁰ reported integral cross sections (ICSs) and energy distributions obtained in a tandem mass spectrometer experiment. A great deal of the theoretical investigation on the title reaction has considered a large enough energy domain to cover the electronic crossing between the energy curves of the states correlating to $H^+ + HD$ and $HD^+ + H$ at about 1.6 eV above the H_2 well minimum. Thus, the pioneering trajectory calculation by Csizmadia *et al.*²¹ yielded DCSs at a collision energy of 3 eV and 4.5 eV. Trajectory surface hopping^{22,23} and adiabatic and nonadiabatic time dependent wave packet (TDWP)^{24,25} or time

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independent close-coupling²⁶ calculations have taken into account the different reactive/nonreactive charge/no-charge transfer mechanisms involved in the process.

The H_3^+ and isotopical variants of the reactive collisions exhibit an overall behaviour which, in principle, corresponds to a complex-forming mechanism as the process proceeds to form the products. The application of different statistical techniques has provided good estimates of both quantum mechanical (QM) calculations and experimental work performed on the system. Thus, for instance, most of the information inferred from Rydberg H-atom time-of-flight spectroscopic measurements^{27–29} have been successfully reproduced^{30,31} by means of a statistical quantum mechanical (SQM) method.^{32,33} Different alternative approaches based on the assumption of the formation of an intermediate complex with a long enough lifetime before its fragmentation proved adequate to describe the dynamics of the process.^{34–39} Changes of the mechanisms governing the reaction as a function on the collision energy regime have been, however, reported since the pioneering investigations on the H_3^+ system. It is generally understood that as the energy increases the process evolves from a complex-forming pathway to a direct reaction.^{20,23,40,41} In those earlier works this transition between different dynamical mechanisms has been observed at the onset of the charge-transfer channels which become energetically open after the electronic crossing mentioned above.^{9,26} In more recent studies on the $\text{H}^+ + \text{D}_2$ and $\text{D}^+ + \text{H}_2$ reactions the deviation of the statistical predictions obtained with a statistical quasiclassical trajectory (SQCT) approach with respect to QM results are observed at much lower energies. In addition, and in spite of the remarkably good agreement found between the SQM and QM rate constants^{4,5} for the $\text{H}^+ + \text{H}_2$ reaction, a comparison at a finer detail at the low energy regime (10^{-6} eV– 10^{-3} eV) revealed significant discrepancies for the DCSs. The system has also served to test approximative semi-classical methods designed in between the quantum and classical description of the reaction dynamics of the process.^{42,43} The apparent success of the statistical treatments for this system has been also questioned by recent experimental work in which binary rate coefficients were measured for the stabilization of $\text{H}^+ - \text{H}_2$ collision complexes by means of a radio frequency ion trap at a temperature between $T = 11$ K and 33 K. The observed behaviour of the rate coefficients for both $j = 0$ and $j = 1$ initial rotational states for H_2 manifested differences with respect to the expected results from models designed on statistical assumptions for the association to form and stabilize H_3^+ complexes.⁴⁴

The above mentioned SQM approach was also employed for the $\text{D}^+ + \text{H}_2$ reaction on Ref. 45 besides TDWP calculations. Reaction probabilities obtained by means of both methods were compared for different values of the total angular momentum J . The overall agreement found for $J = 0$ was accompanied by the apparent failure of the statistical predictions as J increases, a feature which, however, was due to the small number of helicity components employed in the TDWP calculation.⁴⁶ The title reaction has also been investigated by means of the SQCT approach, in combination with a variety of different theoretical methods.⁴⁷ The rate coefficients in terms of the collisional energy obtained with this

quasi-classical version of the SQM approach were found to diverge from purely quasi-classical trajectory (QCT) calculations rapidly beyond $E_c \sim 3 \times 10^{-1}$ eV for processes initiated from different initial rotational states of H_2 . A straightforward comparison for the entire energy range there considered with the time independent quantum mechanical (TIQM) method employed (the ABC code⁴⁸) was, however, not reported, since the QM calculation was limited up to $E_c \sim 0.4$ eV and the SQCT results were only shown from $E_c \sim 10^{-3}$ eV for $j = 0$ and between $\sim 5 \times 10^{-3}$ and 0.5×10^{-2} eV for $j = 1–3$. For those energies in which results obtained with both methods were compared, the statistical rates remain slightly above with the only exception of the lowest energies for the reaction initiated from $\text{H}_2(v = 0, j = 0)$ where the agreement was better. The corresponding thermally averaged rate coefficients of that work were compared with some previous experimental works. In particular, the SQCT values lay within the error bars of the measurements of Ref. 19 up to $E_c \sim 0.18$ eV, and within the experimental uncertainties of some other ion beam techniques for larger energies up to ~ 1 eV.⁴⁷ The comparison of thermal rate constants between 100 and 500 K revealed that the statistical predictions are larger than both QM and QCT results, but are on the contrary, perhaps accidentally, the closest theoretical rates to the measurements by Henchman *et al.*¹⁸

Recently, some of us have carried out TIQM calculations on the $\text{D}^+ + \text{H}_2 \rightarrow \text{HD} + \text{H}^+$ reaction to obtain ICSs and thermal rate constants at low temperature.⁴⁹ The comparison with previous experimental work^{19,50} revealed that the calculation reproduced rate constants beyond a collision energy of 0.006 eV. The independence with E_c of the measured $k(E)$ observed below that value was, however, at odds with the theoretical result and possible shortcomings of the PES employed in the study were invoked. The thermal rate constants obtained with the TIQM method were smaller at $T < 100$ K than statistical predictions reported at Refs. 19 and 51.

In this work, we compare results from Ref. 49 with predictions obtained with the above mentioned SQM approach to analyze the possible validity of a statistical treatment for low values of the collisional energy, a feature which would shed some light regarding the complex-forming nature of the process. In principle, for such regime, the low number of contributing partial waves and energetically open states for the diatoms at both reactant and product arrangements would invite to think that individual capture probabilities at both sides of the reaction could not correspond to a statistical share of the total probability. Therefore, in an attempt to investigate the ultimate dynamical mechanisms which rule the title reaction when E_c decreases, the TIQM results for such energy regime would be analyzed in detail, something that was not previously done in the report by Honvault and Scribano.⁴⁹

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

II. THEORY

Both the TIQM and SQM methods have been extensively described in previous works (see, for instance, (Refs. 52, 32,

and 33 for original reports, respectively, on these two techniques). These two approaches have been applied in common for a better understanding of the dynamics of several atom-diatom reactions such as $\text{N}+\text{H}_2$,⁵³ $\text{O}+\text{OH}$,⁵⁴ $\text{H}^+ + \text{H}_2$,^{4,55,56} and $\text{H}^+ + \text{D}_2$.^{14,31}

Numerical details of the TIQM calculation performed by Honvault and Scribano were given before.⁴⁹ The number of rovibrational states for the reactant and product channels and of helicity components was found to guarantee converged results down to energies within the 10^{-4} eV– 10^{-3} eV range. For rate constants, convergence was obtained for $T \geq 10$ K. The reaction probability for $J = 0$, not shown in Ref. 49, was calculated solving 200 coupled second order differential equations to obtain the coefficients of the expansion for the scattering wave function on the corresponding set of hyperspherical adiabatic states.

The SQM method is based on the assumption of a complex-forming dynamics of the process in which the state-to-state probability between the initial state $vj\Omega$ from the α reactants arrangement and the final state $v'j'\Omega'$ from the product channel α' at the total angular momentum J can be expressed as

$$|S_{\alpha'v'j'\Omega',\alpha vj\Omega}^J(E)|^2 \simeq \frac{P_{v'j'\Omega'}^{J\alpha'}(E)P_{vj\Omega}^{J\alpha}(E)}{\sum_{\alpha''v''j''\Omega''} P_{v''j''\Omega''}^{J\alpha''}(E)}. \quad (1)$$

The individual capture probabilities $P_{vj\Omega}^{J\alpha}$ and $P_{v'j'\Omega'}^{J\alpha'}$ are calculated separately solving the corresponding close-coupled equations by means of the log derivative method between the asymptotic region $R_{\max} = 15 a_0$ and $R_c = 3 a_0$, the capture radius at the entrance of the potential well for each chemical arrangement.³³ Although this value for the asymptotic region was chosen in consistence with the value of ρ_{\max} employed in the TIQM calculation of Ref. 49, the convenience of enlargements of R_{\max} in the SQM calculation will be analyzed in Sec. IV. As for the TIQM calculation, the SQM approach is applied for the process initiated from the ground $\text{H}_2(v = 0, j = 0)$ and the first rotationally excited $\text{H}_2(v = 0, j = 1)$ state have been performed separately considering exclusively even or odd j states, respectively, in the reactant channel.

III. RESULTS

A. Reaction probabilities and cross sections

Reaction probabilities for $J = 0$ in terms of the collision energy, $P(E, J = 0)$, have been calculated for the $\text{D}^+ + \text{H}_2(v = 0, j = 0)$ reaction by means of the TIQM and SQM mentioned in Sec. II. In Fig. 1, both sets of results are compared for energies up to 0.1 eV. The TIQM result exhibits a profile formed by numerous narrow resonances along the entire energy regime under consideration. Although nothing is inferred about the resonance structure of the $P(E, J = 0)$ curve, the statistical predictions provide an overall description of the general trend exhibited by the TIQM probabilities as a function of E_c . Interestingly, the profile of the reaction probability displays plateau regions which are interrupted by sudden increases or decreases due to the energetically onset of the diatom channels $\text{H}_2(v = 0, j)$ and $\text{HD}(v' = 0, j')$ at the reactant and

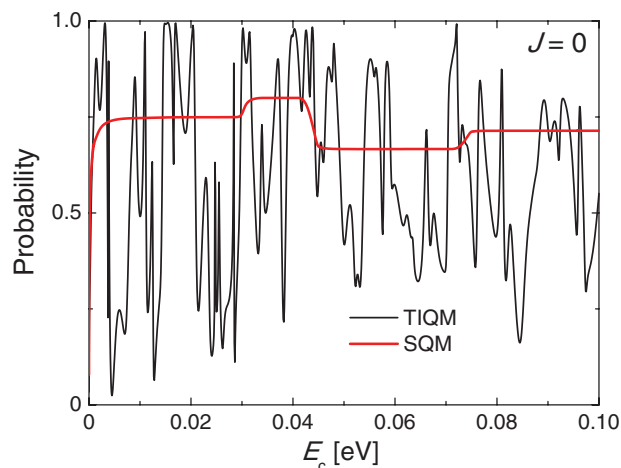


FIG. 1. Reaction probabilities for the $\text{D}^+ + \text{H}_2(v = 0, j = 0) \rightarrow \text{H}^+ + \text{HD}$ reaction at $J = 0$. TIQM results (black line) are compared with statistical predictions (red line).

product arrangements, respectively.⁴⁵ In particular, at the energy region shown in Fig. 1, and considering that (i) only those H_2 rotational states with j even are included in the calculation of the reaction probability for $\text{D}^+ + \text{H}_2(v = 0, j = 0)$ (that is, $\text{H}_2(v = 0, j = 1, 3)$ are therefore excluded), and (ii) $\text{HD}(v' = 0, j' \leq 2)$ states are accessible for all energies, it is straightforward to assign the features at $E_c = 0.0301$ eV and 0.0736 eV to the onset of the $\text{HD}(v' = 0, j' = 3)$ and $\text{HD}(v' = 0, j' = 4)$ states, respectively. In turn, the decrease of the SQM $P(E, J = 0)$ at $E_c = 0.0439$ eV is due to the onset of the $\text{H}_2(v = 0, j = 2)$ state at the entrance channel. From Eq. (1) it is easy to observe that the appearance of contributing rovibrational states $\text{H}_2(v, j)$ as the energy increases, enlarges the denominator and therefore reduces the state-to-state reaction probability within the SQM framework, whereas each new contributing $\text{HD}(v', j')$ state also affects the numerator.

Statistical ICSs for the $\text{D}^+ + \text{H}_2(v = 0, j = 0)$, $\sigma_{j=0}(E)$, and $\text{D}^+ + \text{H}(v = 0, j = 1)$, $\sigma_{j=1}(E)$, reactions have been calculated. The comparison with the TIQM results of Ref. 49 is shown in Figs. 2 and 3, respectively.

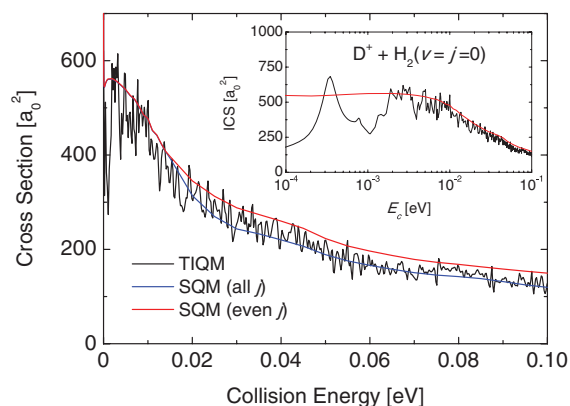


FIG. 2. Integral cross sections for the $\text{D}^+ + \text{H}_2(v = 0, j = 0) \rightarrow \text{H}^+ + \text{HD}$ reaction. TIQM results (black line) are compared with statistical predictions in which only even (red lines)/all (blue lines) rotational states of $\text{H}_2(v = 0, j)$ are taken into account. The inset displays the same results on a log scale for the sake of clarity at the low energy regime. See text for details.

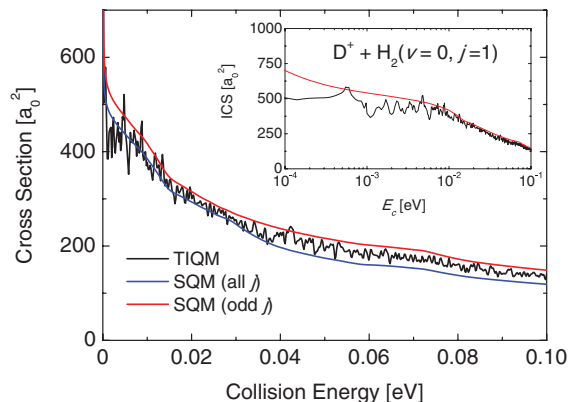


FIG. 3. Same as Fig. 2 for $D^+ + H_2(v=0, j=1) \rightarrow H^+ + HD$ reaction. SQM results are in this case for odd (red lines)/all (blue lines) rotational $H_2(v=0, j)$ states.

As already reported for the case of $H^+ + H_2^4$ the cross sections exhibit a profile dominated by the presence of a large number of resonances. A not excessively large number of contributing partial waves could certainly explain the highly structured ICSs obtained by means of the TIQM calculation. The maximum value of the total angular momentum J_{max} ranges from 5 at $E_c = 10^{-4}$ eV up to about 35 for the largest energy considered in this work, $E_c = 0.1$ eV. In this sense the apparent smoothing observed as the energy increases in the cross sections shown in Figs. 2 and 3 seems to be related with the larger values of J_{max} when E_c becomes higher. For the $D^+ + H_2(v=0, j=0)$ reaction in particular, the TIQM ICSs still present surviving resonances at low values of the collision energies: see for instance at the inset of Fig. 2, the structure at the 10^{-3} to 10^{-2} eV range and more specially the noticeable maximum peak at $E_c \sim 3.5 \times 10^{-4}$ eV.

The TIQM calculation explicitly separates the parity of the H_2 rotational states with independent runs for odd and even j states. Moreover, no inclusion of two identical product channels was taken into consideration. Both features were accounted for in the SQM calculation. In Fig. 2, for example, the corresponding results $\sigma_{SQM}(E)$ are shown with the red line. The agreement with the TIQM calculation is quite noticeable with a decent reproduction on average of the trend followed by the TIQM cross section. It is worth mentioning that if all H_2 states are included in the sum of the denominator of Eq. (1) the comparison with the TIQM results certainly improves beyond the energy at which $H_2(v=0, j=1)$ becomes energetically accessible, since the SQM cross sections get smaller.

The behaviour at the low energy regime of the cross sections, shown in the inset of Fig. 2, reveals that the statistical prediction which remains as a reasonable counterpart for the TIQM cross sections down to $E_c \sim 2 \times 10^{-3}$ eV, crosses through the resonance peak and stays, at the log scale for the energies employed in the inset of Fig. 2, along a plateau extended between $\sim 10^{-4}$ and 4×10^{-2} eV.

For the $D^+ + H_2(v=0, j=1)$ case (see Fig. 3), the cross sections exhibit a similar behaviour at the larger energies regime considered in this study $E_c > 10^{-2}$ eV. Thus,

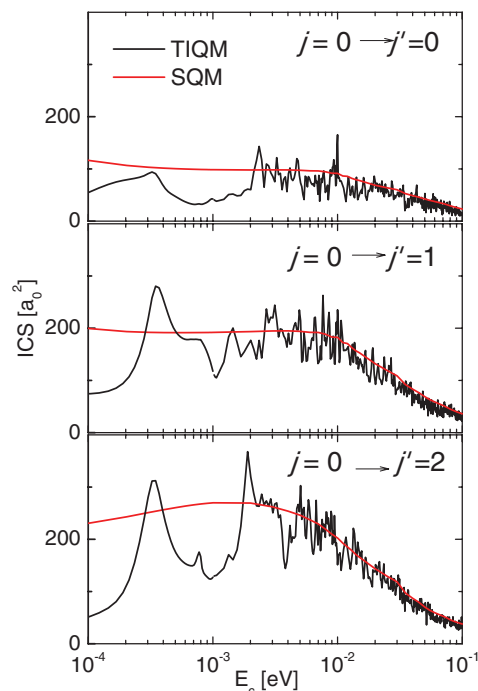


FIG. 4. State-to-state rate coefficients in terms of E_c for the $D^+ + H_2(v=0, j=0) \rightarrow H^+ + HD(v'=0, j'=0-2)$ reaction.

the agreement between TIQM and SQM ICSs is of the same level as for the reaction initiated from the excitationless H_2 . The option which includes all rotational states of molecular hydrogen for the statistical calculation remains even below the TIQM cross sections and never matches the only odd $H_2(v=0, j)$ states restricted version due to the presence of the $j=0$ state which is energetically open when the reaction initiates from $H_2(v=0, j=1)$. Resonances around $\sim 3.5 \times 10^{-4}$ eV seem to be less pronounced than for the $H_2(v=0, j=0)$ case. Between $E_c \sim 5 \times 10^{-3}$ eV and $\sim 10^{-2}$ eV peaks are more sparse in $\sigma_{TIQM}(E)$ which displays a structure just slightly overestimated by the statistical predictions. Precisely, at this low energy regime analogous differences were observed between rate coefficients in terms of the collision energy obtained by means of the same method and the experimental result by Gerlich.¹⁹

It is also interesting to analyze the behaviour of the state-to-state ICSs for the corresponding $D^+ + H_2(v=0, j) \rightarrow HD(v'=0, j'=0-2) + H^+$ processes. The study of Ref. 49 certainly includes the TIQM cross sections shown here but the only energy range depicted there in detail excluded energies below 10^{-2} eV. In Figs. 4 and 5, we present these results in terms of the energy on a logarithmic scale. Notice that the case in which the final rotational state of the HD unit is $j'=3$ is not included in the comparison given that remains as a close channel for the energies investigated in detail in the above mentioned figures.

The origin of the resonance seen for the reaction initiated from the excitationless H_2 at $E_c \sim 3.5 \times 10^{-4}$ eV is uncertain but seems to be more pronounced for those processes in which the final HD is produced with some rotational excitation $j' > 0$. There is also a distinct behaviour at the lowest energies depending on the rotational state of the products: For

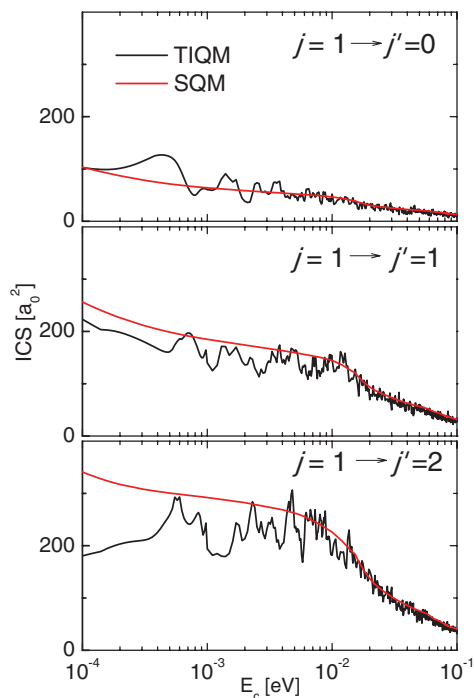


FIG. 5. Same as Fig. 4 for $D^+ + H_2(v = 0, j = 1)$.

$j' = 0, 2$ the TIQM cross sections are remarkably smaller than the observed result for $j' = 1$. A similar situation is found for the reactions initiated from $H_2(v = 0, j = 1)$ (see Fig. 5).

The corresponding SQM predictions for these state-to-state $\sigma(E)$ have been also included in Figs. 4 and 5 for comparison. In this case the only results shown in the figure corresponds to the calculation performed by considering just one type of rotational states, and no comparison with the run in which both odd and even j rotational states are taking into account in the denominator of Eq. (1) is established. As already observed for the case of the initial-state-selected cross sections, the agreement for the higher collision energies considered in the present work is quite reasonable. In all cases, the statistical values constitute a decent counterpart which successfully describes the overall trend found for the TIQM results. The agreement observed for the $j = 0 \rightarrow j' = 1$ and $j = 1 \rightarrow j' = 1$ transitions between the H_2 and HD rotational states is remarkable.

The lowest energy considered in this comparison between TIQM and SQM cross sections, 10^{-4} eV is certainly far of the Wigner regime. A precise description of the energy regime at which reactive cross sections are expected to vary as $E_c^{-1/2}$, the so-called Wigner regime, was out of the scope of the present study.

B. Rate constants

TIQM rate constants up to $T = 100$ K for the present reaction have already been reported in Ref. 49. In that work, Honvault and Scribano concluded that their results for the $j = 0$ case were about between two and four times smaller than the statistical predictions of McCarroll,⁵¹ for the reaction initiated with $H_2(v = 0, j = 1)$ however the TIQM rates

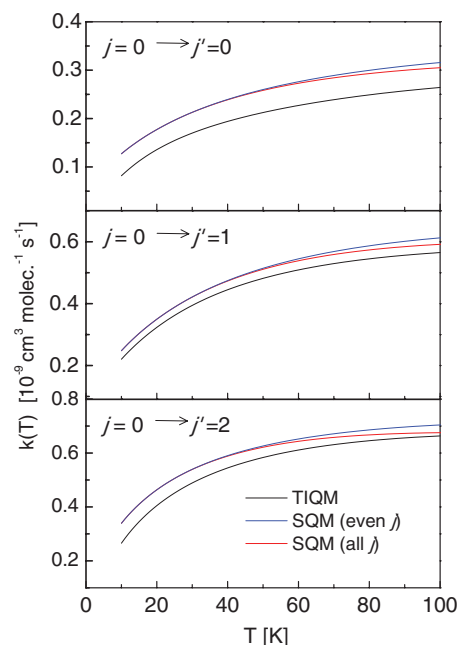


FIG. 6. State-to-state rate constants for the $D^+ + H_2(v = 0, j = 0) \rightarrow H^+ + HD(v', j' = 0 - 2)$ reaction. TIQM results in black line are compared with SQM predictions with only $H_2(v, j \text{ even})$ states in the calculation (blue line) or all rotational states (red line).

were found larger than those statistical results. In turn, the value at $T = 100$ K reported by Jambrina *et al.*⁴⁷ is in good agreement with the rate constant of Ref. 49. For higher values of T , previous experimental reports^{15,19,50} were inferred to be consistent with the TIQM results. The state-to-state $k(T)$ for the $D^+ + H_2(v = 0, j = 0) \rightarrow DH(v' = 0, j') + H^+$ and $D^+ + H_2(v = 0, j = 1) \rightarrow DH(v' = 0, j') + H^+$ reactions are shown in Figs. 6 and 7, respectively, for $j' = 0-2$ in comparison with the presently employed SQM approach. The rate constants for $j' = 3$ are much smaller and are not shown in those figures.

As in the case of the $H^+ + H_2$ reaction,^{4,56} the statistical predictions are found to reproduce correctly the qualitative behaviour of the TIQM results as a function of the temperature. In addition, the comparison with the TIQM values shows that the quantitative agreement is also remarkable. Thus, for the reaction initiated from $H_2(v = 0, j = 0)$, the largest discrepancies are found for the transition to the $HD(v' = 0, j' = 0) + H^+$ product arrangement for which the $k_{SQM}(T)/k_{TIQM}(T)$ ratio goes from ~ 1.6 at $T = 10$ K to ~ 1.2 at $T = 100$ K. Most favourable cases are $j' = 1$ and 2 for which such ratio remains almost constant around ~ 1.1 or evolves from ~ 1.3 at $T = 10$ K to ~ 1.1 at $T = 100$ K, respectively. For $j' = 3$, the TIQM rates are larger than the statistical counterparts with differences between both sets of results which, as in the case of $j' = 0$, make the above mentioned ratio to range between ~ 1.7 at $T = 35$ K and ~ 1.1 at $T = 100$ K.

A similar comparative analysis of the thermal rate constants for the $D^+ + H_2(v = 0, j = 1) \rightarrow HD(v', j' = 0-2) + H^+$ reaction (shown in Fig. 7) reveals also an interesting agreement between the TIQM and SQM results. It is worth noticing that the best accord is found for the process of HD formation in its ground rovibrational state $v' = j' = 0$.

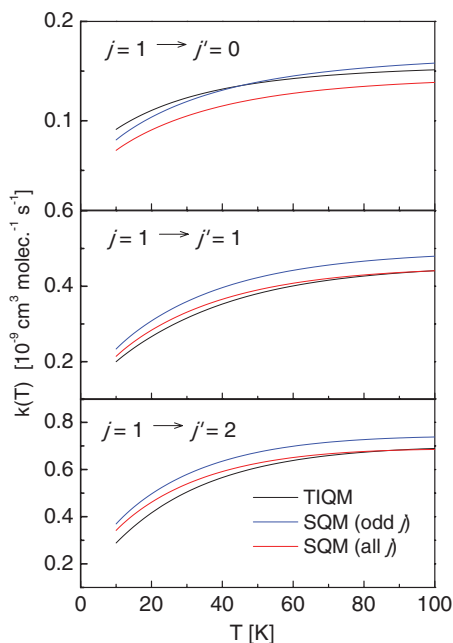


FIG. 7. Same as Fig. 6 for $D^+ + H_2(v = 0, j = 1) \rightarrow H^+ + HD(v', j')$ reactions. SQM results with only $H_2(v, j \text{ odd})$ rotational states are in blue line.

The $k_{\text{TIQM}}(T)$ constant is larger (about ~ 1.13 times at its maximum at $T = 10$ K) than the statistical $k_{\text{SQM}}(T)$ result up to $T \sim 45$ K. Beyond that temperature, the $k_{\text{SQM}}(T)/k_{\text{TIQM}}(T)$ ratio never exceeds 1.05. The statistical state-to-state rate constants for the production of rotationally excited $HD(v' = 0, j' > 0)$ from $H_2(v = 0, j = 1)$ are larger than the TIQM results for the whole temperature range here considered. The above mentioned ratio remains almost constant around ~ 1.1 for $T > 40$ K, for the other cases, $j' = 1, 2$, and only larger deviations (not more than 1.17) are observed at the lowest temperatures.

In a similar attempt as done before for the ICSs (see Figs. 2 and 3) to evaluate the differences when the statistical calculation are performed without any restriction with respect to the H_2 rotation, results when all possible $H_2(v, j)$ states are taking into account are shown in Figs. 6 and 7. The rate constants calculated within this condition do not differ too much from the the results of the only-odd j SQM calculation for $H_2(v = 0, j = 0)$ and only start to diverge at the larger temperatures. More noticeable differences are seen for the $H_2(v = 0, j = 1)$ case (see Fig. 7) for which the two possible statistical rate constants seem to display an almost constant deviation at the entire temperature range.

The comparison between the TIQM and SQM state specific rate constants for the initially-selected $D^+ + H_2(v = 0, j = 0, 1)$ reactions are shown in Fig. 8. As expected for the already discussed results at the state-to-state level, the statistical $k_{\text{SQM}}(T)$ constitute an acceptable counterpart of the corresponding $k_{\text{TIQM}}(T)$ rates. Thus, for $j = 0$ the SQM values are only ~ 1.26 times larger than the TIQM constants at $T = 10$ K and become only 1.1 times larger at $T = 100$ K. On the other hand, for the $j = 1$ case the comparison is even better, since $k_{\text{SQM}}(T)$ is only about 1.18 times larger than $k_{\text{TIQM}}(T)$ at $T = 10$ K and decreases up to 1.08 times larger at $T = 100$ K.

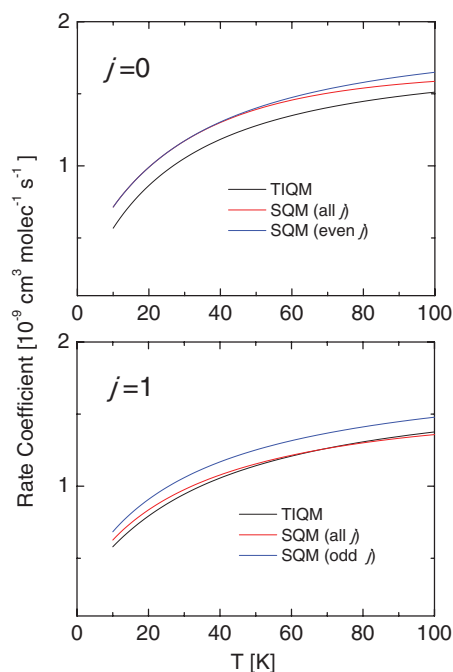


FIG. 8. Initial state selected rate constant for the $D^+ + H_2(v = 0, j) \rightarrow H^+ + HD$ process with $j = 0$ (top panel) and $j = 1$ (bottom panel) calculated by means of the TIQM method (black line) and the SQM approach. The statistical calculations with specific rotational parity (or not) of H_2 are also included. See text for details.

The most appreciable consequence of summing over all reactants rotational states in the SQM calculation is observed for the $D^+ + H_2(v = 0, j = 1) \rightarrow HD + H^+$ case (see bottom panel of Fig. 8). The statistical output and the corresponding TIQM $k(T)$ rates get almost at top of each other. When the reaction is, however, initiated with H_2 at its ground state the differences become only noticeable beyond $T = 60$ K with the extra inclusion of the $H_2(v = 0, \text{odd } j)$ states, not contemplated when only even j states of the H_2 reactants are taken into account, making the $k_{\text{SQM}}(T)$ rates to decrease as the temperature increases.

The comparison reported here with the TIQM rate constants seems to improve the performance observed for some other statistical methods applied to the title reaction. Thus, differences between the SQM approach and the $k_{\text{TIQM}}(T)$ constants are smaller than those reported for the model based on a modified Langevin approach proposed by McCarroll.⁵¹ In this method, the rate coefficients are calculated by means of a Boltzmann integration of the total reaction probability estimated through the number of accessible states under an effective isotropic potential. The strict Langevin model establishes a value which is too large ($2.1 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) in comparison with both the $k_{\text{SQM}}(T)$ and $k_{\text{TIQM}}(T)$ results at the 10–100 K range. Analogously, the statistical model proposed by Gerlich^{19,50} based on classical trajectory calculations is found to have some difficulties to describe the TIQM prediction at the low temperature regime. The comparison with values from the analytical formula proposed for authors of Ref. 50 for the $30 \text{ K} \leq T \leq 130 \text{ K}$ range is shown in Table I of the thermal rate constants calculated in this work with the TIQM and SQM methods averaging the rate constants for the

TABLE I. Comparison of the present SQM thermal rate constants (in $10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) with the TIQM results of Ref. 49 and with those by Gerlich and Schlemmer.⁵⁰

T	TIQM	SQM	Ref. 50
10	0.5673	0.7143	
20	0.8680	0.9905	
30	1.0520	1.1729	
40	1.1728	1.2989	1.4400
50	1.2550	1.3873	1.4824
60	1.3135	1.4509	1.5111
70	1.3574	1.4982	1.5318
80	1.3919	1.5350	1.5475
90	1.4200	1.5646	1.5597
100	1.4435	1.5891	1.5696

$\text{H}_2(v=0, j=0)$ and $\text{H}_2(v=0, j=1)$ initial states. In spite a better agreement at much higher temperatures is suggested, rates from the statistical approach of Ref. 50 do not display the trend as a function of T of the QM results. The present SQM calculation on the contrary yield thermal rate constants with the correct dependence as the temperature decreases. In this sense it is worth pointing out that the $k_{\text{SQM}}(T)$ results for the $\text{H}^+ + \text{H}_2$ reaction display the right trend at low values of the temperature, as opposed to the predictions by some other statistical techniques.^{39,57}

There are not many measurements of the thermal rate constant for the title reaction at the temperature range considered in this work. As shown in Ref. 47, the $\text{D}^+ + \text{H}_2$ process has been experimentally studied at much more extent for higher values of T . Fehsenfeld *et al.*¹⁵ reported a value larger than $0.7 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at $T = 80 \text{ K}$ and almost independent value with respect to the temperature of about $1.0 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ with error bars of $+0.5/ - 0.25 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ for the range $100 \text{ K} < T < 287 \text{ K}$. Both experimental results remain below the output of both theoretical results obtained in the present study. The $k_{\text{SQM}}(T)$ results overestimate the measured rate constants, as observed beyond $E_c \sim 0.04 \text{ eV}$ in the comparison established by Jambriña *et al.*⁴⁷ for rate constants as a function of the energy for the title reaction calculated by means of the SQCT approach and measurements from ion beam investigations.

IV. DISCUSSION

The analysis of the TIQM ICSs at the low energy regime has revealed an interesting distinct behaviour depending on the precise rotational excitation at both the H_2 and HD fragments at the reactant and product arrangements, respectively. According to the initial state resolved cross sections (see Figs. 2 and 3) the formation of HD as the collision energy decreases close to 0 is favoured when the reaction is initiated from $\text{H}_2(v=0, j=1)$ as compared to the process from H_2 at its ground rovibrational state. Thus, the $\sigma_{j=1}$ cross section is more than 2 times larger than $\sigma_{j=0}$ at $E_c = 10^{-4} \text{ eV}$. However, the $\text{D}^+ + \text{H}_2(v=0, j=0) \rightarrow \text{HD} + \text{H}^+$ reaction is found to be mediated by the existence of an almost isolated resonance between 10^{-4} eV and 10^{-3} eV which, at the log

scale used in the figure, looks markedly different to the profile of the cross sections for $E_c > 10^{-3} \text{ eV}$ characterized by numerous narrow peaks. This feature is consistent with the energy difference between rotational states of the H_3^+ complex, about 1 meV. The inspection at the state-to-state level suggests that this peak appears as long as the HD is produced with some content of rotational energy, $j' > 0$. This preference for certain rotational excitation either at the H_2 reactant or HD product diatoms, or even in both cases, which is also manifested in the corresponding rate constants, could have its origin in part on the anisotropic components of long range charge-quadrupole and charge-induced dipole dispersion energies.

Reactive resonances at such low energy regime have been widely studied before given the important role which these features may play in cold and ultracold processes.⁵⁸ Their physical existence is nevertheless a subtle issue given the extreme dependence of the dynamics of the reactions at such extreme conditions on the PES employed in the calculation.⁵⁹ Observed discrepancies between TIQM results and rate constants measured in ion beam experiments at low values of the collision energy have been attributed to possible deficiencies on the description of the long range terms of the presently used PES.¹² Analogously, as already discussed in the Introduction, differences in some dynamical attributes for the $\text{H}^+ + \text{D}_2 \rightarrow \text{HD} + \text{D}^+$ reaction were found when two different potentials were employed in the calculations at higher collision energies.¹⁴ The observed resonances observed here and for the scattering reactions for the H_3^+ system⁴ can be directly related with $\text{H}^+ - \text{H}_2$ radiative association processes.^{44,60} In recent experimental radio frequency ion trap investigations, the deviations from the expected statistical behaviour were tentatively attributed to the rather low number of states accessible to the H_3^+ complex at the temperature regime (11 K–33 K) considered there. In order to elucidate the issue more QM calculations on sufficiently precise PESs are required. Work in this direction is already in progress.

Besides the numerical limitations of TIQM results from Ref. 49 already discussed in Sec. II, the definition of a correct asymptotic region in the SQM calculation, especially for low collision energies, becomes a crucial issue. The choice of the presently used value for the R_{max} has been made in consistency with the previous study by Honvault and Scribano,⁴⁹ and was found to be adequate for other comparisons between both methods for $\text{H}^+ + \text{H}_2$ and isotopic variants at energies down to 0.1 eV. However, as revealed for the reaction $\text{D}^+ + \text{H}_2(v=0, j=0)$ by Fig. 9, a proper convergence of the SQM cross sections at much lower values of E_c requires of extensions of the initially adopted value, $15 a_0$. Thus, R_{max} has to be enlarged up to $\approx 25 a_0$ for $E_c \approx 10^{-3} \text{ eV}$ and up to $\approx 70 a_0$ for $E_c \approx 10^{-4} \text{ eV}$. The resulting values of the SQM cross sections then start to deviate from the TIQM results following an almost constant law in the double logarithmic scale of Fig. 9 with decreasing energy. This is precisely the behaviour one would expect in order to produce rate coefficients with no dependence on the energy as observed at the experimental work by Gerlich.¹⁹

The comparison between the present statistical predictions for $\text{D}^+ + \text{H}_2(v=0, j=0)$ and the measured rate

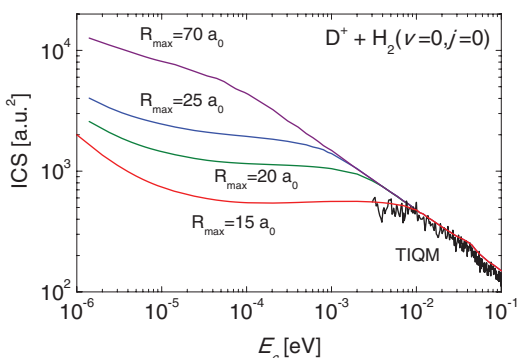


FIG. 9. Convergence test of the cross sections for $D^+ + H_2(v=0, j=0)$ obtained with the SQM approach for different values of R_{max} . TIQM results⁴⁹ are shown for comparison.

coefficients is shown in Fig. 10. The figure reveals a remarkably good agreement between the statistical approach and experiment up to 10^{-3} eV, the lowest energy at which values are reported in Ref. 19, although SQM results are extended up to $E_c \approx 10^{-4}$ eV, an energy range for which convergence is guaranteed once the asymptotic range is extended up to $R_{max} = 70 a_0$. The differences found between the TIQM result and the experiment could possibly have their origin at the maximum value of the hyperspherical coordinate, ρ_{max} , noticeably lower than the maximum distance of the statistical calculation. Work in order to clarify the issue is now in progress.

The calculation of the rate constants with a larger asymptotic region within the SQM approach also leads to results which hardly depend on the temperature beyond 10 K. At this specific value of T , the SQM result for $D^+ + H_2(v=0, j=0)$ with $R_{max} = 70 a_0$ is $1.80 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, $1.84 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at $T = 50$ K and $1.87 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at $T = 100$ K. Differences with respect to the predictions obtained with $15 a_0$ and $25 a_0$ are $\sim 60\%$ and $\sim 11\%$, respectively, at $T = 10$ K and reduce to $\sim 40\%$ and $\sim 6\%$ at $T = 20$ K, respectively.

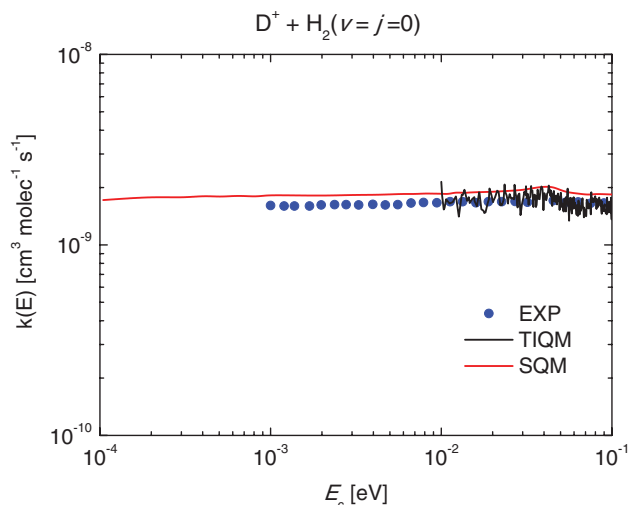


FIG. 10. Rate coefficients as a function of the collision energy for $D^+ + H_2(v=0, j=0) \rightarrow HD + H^+$ calculated with the SQM approach compared with experimental¹⁹ and TIQM⁴⁹ results.

Despite previous evidences of an apparent deviation from a purely statistical behaviour at larger energies for different isotopical variants of the H_3^+ reactive scattering processes, present results open the debate regarding the possible complex-forming nature of the reaction at the low energy regime. As reported for the ortho-para conversion of the $H^+ + H_2$ reaction,^{4,56} ICSs obtained by means of the SQM provide reasonably good description of the QM results. SQM rate constants are found in both quantitative and qualitative good accord with the corresponding $k_{\text{TIQM}}(T)$ counterparts, displaying the correct behaviour at low temperatures ($T < 30$ K). The above discussed capability of the SQM approach to correctly reproduce the experimental rate coefficients (see Fig. 10), thus extending the agreement observed for the most dynamically biased statistical theory by Gerlich⁵⁰ with measured values, also constitute a solid argument in favour of the formation of an intermediate complex at such temperature regime. It is worth mentioning that statistical approaches are also subject to possible deficiencies on the long range region of the PES, where the actual calculations are performed since the collision complex region is usually neglected in these sort of approaches, but the improvement observed as R_{max} increases seems to discard that possibility as the main reason for the apparent failure of TIQM calculations to describe the experiment.⁴⁹

V. CONCLUSIONS

The low energy regime between 10^{-4} eV and 0.1 eV of the $D^+ + H_2 \rightarrow HD + H^+$ reaction has been studied by means of a SQM approach and compared with previously reported TIQM results. ICSs for reactions initiated from $H_2(v=0, j=0)$ and $H_2(v=0, j=1)$ are characterized, according to the TIQM study, by a dense structure of narrow resonances beyond $E_c \sim 10^{-3}$ eV. In addition, for $j=0$, a prominent peak is observed between 10^{-4} and 10^{-3} eV, which has its origin in those reactions forming rotationally excited $HD(v'=0, j' > 0)$. The statistical predictions reproduce reasonably well the overall trend of the cross sections and provide a quantitative counterpart of the TIQM results with the same temperature dependence between 10 and 100 K. Test calculations performed with the statistical approach suggest the convenience of a sufficiently large asymptotic region to study the low energy range. Thus, the agreement observed with experimental rate coefficients in terms of the energy down to 10^{-3} eV invites to think that the complex-forming mechanism seems to play then an important role at such energy and temperature regimes.

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