Universality in the cold and ultracold dynamics of the barrierless $D^+ + H_2$ reaction.

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We have calculated quantum reactive and elastic cross-sections for the collision $D^+ + \text{para-H}_2(v=0, j=0) \rightarrow H^+ + HD$ using the hyperspherical quantum reactive scattering method [Chem. Phys. Lett., 1990, 169, 473]. The $H^+_3$ system is the prototype of barrierless ion-molecule reactions, apart from its relevance in astrochemistry. The considered collision energy ranges from the ultracold regime, where only one partial wave is open, up to the Langevin regime, where many of them contribute. At very low kinetic energies, both an accurate description of the long-range (LR) region in the potential energy surface (PES), and long dynamical propagations, up to distances of $10^5 \ a_0$, are required. Accordingly, calculations have been carried out on the PES by Velilla et al. [J. Chem. Phys., 2008, 129, 084307] which accurately reproduces the LR interactions. Besides, the hyperspherical methodology was recently modified in order to allow the accurate inclusion of LR interactions while minimizing the computational expense. Such implementation is shown particularly suitable for systems involving ions, where the $\sim R^{-4}$ behavior largely extends the range of the potential. We find a reaction rate coefficient which remains almost constant in a kinetic energy range of more than ten orders of magnitude. In particular, the value reached in the Wigner regime, where only one partial wave is open, is paradoxically the Langevin classical value (within a few percent) expected at high energies. Results are discussed in terms of universality and related to the recently published quantum defect theory by Jachymski et al. [Phys. Rev. Lett., 2013, 110, 213202]. In this regard, the system has small exothermicity and a low number of channels, what allows to test such model in a case where the loss probability at short range is appreciably far from unity. The latter parameter has been rationalized using statistical model assumptions and related to the products statistical factor.

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INTRODUCTION

The increasing availability of cold and ultracold samples of molecules has aroused a great interest in understanding chemical reactions occurring at very low temperatures. Given the easiness in the production of (ultra-)cold alkali metal dimers, attention has mainly focused in reactions including alkali atoms [37, 61, 80, 81, 93, 94]. This way, in a landmark experiment, reaction rates for atom+diatom and diatom+diatom collisions involving fermionic $^{40}\text{K}^{87}\text{Rb}$, at temperatures less than 1 $\mu$K, were recently measured [64]. In contrast, advances in the analysis of other type of reactions are still hampered by the lack of versatile methods to produce molecules at low temperatures and the very low densities achieved. Luckily, emerging experimental techniques promise to provide detailed information on cold bimolecular collisions [8, 9, 11, 12, 16, 51, 62, 72, 73, 88, 99]. New experimental approaches developed by Narevicius and coworkers [31, 62, 72, 73], appear highly promising since they allow the study of reactions other than those involving alkalis or possessing permanent electric dipole moment, while reducing the considered temperatures in more than three orders of magnitude and hence to ultracold regime ($T<1$ mK).

With regard to the title system, recent experiments have been able to stabilize $H^+_3$ complexes resulting from the collision $H^+ + H_2$ in ion traps for energies as low as 11K [23]. Experiments to determine state specific rate coefficients at very low temperatures are within the reach of current rf ion trap technology and may be performed in a close future. The title reaction may thus provide us with a good chance to check and extend our predictive power from the explored thermal regime, where ab initio reaction dynamics is routinely applied, to the low energy regime where such methodology should fail due to the lack of accuracy. In the limit, the deep ultracold regime is governed by Wigner laws [70] and can be de-
scribed in terms of the scattering length. Paradoxically, the extreme sensitivity of such parameter to the details of the potential energy surface (PES), and the action of the surface as a whole, makes extremely difficult to predict it theoretically or, conversely, to deconvolute from its measurement the underlying interactions. Given the resonant nature of the scattering length, it largely varies with slight changes of the interaction potential whenever a bound state occurs in the vicinity of the threshold. Only for very light atoms like metastable He [63, 87], or very particular atom-atom combinations [45] it is nowadays possible to obtain the experimental scattering length from “ab initio” calculations. Actually, in the atomic realm the electronic potential curves are modified “ad hoc” according to the experimentally measured scattering length in order to ensure that they are accurate enough to be used in dynamical studies at low kinetic energies [78].

While our knowledge on the behavior of ultracold atomic systems has impressively increased during the last decades, it remains as an open question to what extent this might be achieved for atom+diatom systems, where even the experimental determination of complex scattering lengths will have to wait [89, 104, 115]. Ab initio methodology applied to explore the ultracold regime in an atom+diatom system like the title system is not expected to have real predictive power. Instead, in the spirit of the seminal paper by Gribakin et al. [27] we will face this study as an effort to unravel the “typical” scattering length that one may expect. In that reference, the authors obtain a simple analytical formula which uncovers the way the atomic interaction determines the scattering length for a potential curve (PES in a wide sense) behaving as \(-C_n/R^n\) at LR. Their expression, can be schematically written as \(a = \bar{a}[1 - \tan(\pi/n - 2) \tan(\Phi - \Phi_0)]\), where \(\bar{a}\), the mean scattering length, does only depend on the LR behavior, and is proportional to a power of the mass and the \(C_n\) parameter. However the semiclassical phase at zero kinetic energy, \(\Phi\), depends on the shape of the potential at any \(R\), being extremely sensitive to small changes of the potential when the number of bound levels is large.

In this way, with continuous change of the parameters of the potential, the phase term, which strongly depends on the details of the potentials, makes the scattering length oscillate very quickly about \(\bar{a}\), whose dependence on the potential is weak; the latter thus deserves the name of of typical or mean scattering length. In the absence of bound states close to threshold, \(a\) basically coincides with \(\bar{a}\), what leads to the paradoxical idea of universality: the result of the collision depends exclusively on the LR behavior and not on the details of the strong short-range chemical interactions.

In contrast to the situation in the ultracold regime commented on above, collisions in the range of ~ 1 K lie within the limits of what can be predicted using the conventional theoretical tools. Far from being a necessary stop in our route from the thermal to the ultracold regime, they have an interest on their own. Apart from being of astrophysical relevance, they report the combined influence of LR and short-range (SR) interactions. While the ultracold scenario favors LR interactions, leading to universality in some extreme cases [45], the thermal regime and its higher kinetic energies makes SR chemical forces prevail. In the cold regime both SR and LR interactions play the game and the use of a balanced PES which describes accurately the whole configuration space is required. Sometimes, their roles may be independent enough to allow to associate trends in the behavior to different regions of the PES, offering insight in the underlying dynamics [53].

Focusing on the title system, reactions of ions with neutrals do not commonly have a significant barrier and, due to their LR attractive potentials \((n = 4)\), exhibit large cross sections. This renders them especially relevant at the low temperatures typical of the interstellar medium (see refs. [82, 104, 117] and references therein). In the past decades, much experimental effort has been dedicated to extend the temperature range down to a few K. The difficulties associated with the handling of small relative translational energies in ion–molecule reactions have been overcome through the use of supersonic jets [29, 60, 74, 75], guided and merged beams, and ion traps [15, 20, 83, 85]. In particular, special attention has been paid to the study of hydrogen-like ions and specifically to the investigation of the \(H^+_3\) system.

The \(H^+_3\) molecule is the most abundant triatomic ionic species in dense interstellar clouds [50] and in many cold hydrogen plasmas [33, 57]. This ion is also formed as a strongly bound intermediate in collisions of \(H^+\) with \(H_2\). Due to its apparent simplicity, the system \(H^+_3\) constitutes a prototype in the field of ion-molecule reactions. As a result it has been a favorite of both theoretical and experimental studies. Depending on the total energy, collisions of protons with hydrogen molecules can have different outcomes, including rovibrational energy transfer, charge transfer, dissociation of the molecule into its atomic components, as well as radiative association leading to stable \(H^+_3\). At energies below \(\approx 1.7\) eV proton exchange is the only reactive channel and we will limit our attention to this particular process. Early calculations starting in the seventies [7, 17, 22, 51, 71] disclosed the main characteristics of the reaction dynamics. It was seen to evolve from a low energy behavior, dominated by capture into a strongly interacting complex, followed by a statistical breakdown of the three-atom complex, to the appearance of dynamical constraints with growing energy, caused by increasingly direct collisions with shorter interaction times. These short interaction times do not allow for a complete randomization of the energy, angular momentum, and nuclear scrambling within the reaction intermediate. These calculations, based on sim-
ple statistical models, semiempirical PESs, and a limited number of classical trajectories, were able to account reasonably well for the available experimental values of cross sections and rate coefficients [18, 30, 60, 63, 90], although not without considerable discrepancies.

Over the last two decades, great progress was achieved in the construction of accurate potential surfaces for the $H_2^+$ system [2, 6, 38, 47, 52, 88, 89] and in the development of gradually more rigorous theoretical approaches for the investigation of the nuclear motion. Refined statistical treatments, exhaustive quasiclassical trajectory (QCT) calculations, and time independent (TI) as well as time dependent wave-packet (TDWP) quantum mechanical (QM) methods of varying accuracy were applied to the study of the $H^+ + H_2$ reaction dynamics (see for instance Refs. [4, 5, 10, 24, 25, 28, 41, 43, 55, 82, 95–98 and references therein). Many of these theoretical works were centered on methodological aspects, emphasizing the comparison between different approaches. As a result of these studies it became clear, that despite the apparent simplicity of the reaction considered, all theoretical methods met with problems for the description of its dynamics.

Of all the possible isotopic variants of the $H^+ + H_2$ reaction, that of the deuteron with $H_2$ is exothermic due to the different zero-point energies (ZPE) of reactants and products and thus it is appropriate for a study at the cold and ultra-cold energy regimes. The isotopic substitution allows for a straightforward identification of reactants and products using methods of mass spectrometry. In addition, $D^+ + H_2$ can play an important role in the unusual deuterium fractionation observed in many cold space environments [21, 83, 91]. In fact, isotope selective effects due to deuterated variants of the $H^+ + H_2$ reaction are observable even in room temperature discharges of $H_2/D_2$ mixtures [44].

In the present work, we have calculated quantum reactive and elastic cross-sections and rate coefficients for the collision $D^+ + \text{para-}H_2 \rightarrow H^+ + \text{HD}$ using the hyperspherical quantum reactive scattering method [54]. We have considered collision energies ranging from the ultracold regime, where only one partial wave is open, to the Langevin regime, where many of them contribute. Following the classical and venerable Langevin model, it is expected that barrierless ion-neutral reactions, associated to potentials varying as $R^{-4}$ at LR, will display a constant reaction rate coefficient at high energies (see below). At the same time, the Wigner threshold laws predict also a constant value at very low collision energies. However, the latter does not state whether its value would be high or null, or if it coincides with the Langevin high energy limit. The way both rates (for high and low energy) are related was to be determined. As it will be shown, they basically coincide for the title system, leading to a nearly constant rate coefficient in the whole considered energy range.

At very low kinetic energies, LR interactions (usually disregarded in both PESs and dynamical calculations) are essential, as they determine the amount of incoming flux which reaches the short range region where rearrangement may occur. Both accurate descriptions of the LR region in the PES, and long dynamical propagations (up to distances of hundreds of thousands of a.u.) are thus required. Among the existing PESs for the title system, that by Velilla et al. satisfies the first requirement since it accurately reproduces the LR interactions [88]. The second requirement is fully satisfied by the hyperspherical methodology, recently modified to allow the accurate inclusion of LR interactions while minimizing the computational expense [53].

In two recent works, the dynamics of the title system was analyzed for energies above the cold regime [26, 30] using the same PES. The hyperspherical quantum reactive scattering method [54] was also used although with an implementation that is usually employed in the study of thermal and hyperthermal reaction. In their approach, the propagation is also carried out in hyperspherical coordinates but up to a hyperradius which is large enough for the potential energy to be negligible in comparison with the collision energy. The use of such implementation would be infeasible in the energy regime considered in this work. In fact, the authors of Ref. [30] had problems to converge the lowest energies they considered (on the order of 10 K) and were forced to extend the propagation up to $\rho=40$ a.u. As we will show, small methodological changes in the hyperspherical method allow the convergence of calculations for much lower kinetic energies at a reasonable computational expense [53]. These changes are used for the first time in the present work in order to converge scattering results corresponding to energies as low as $10^{-8}$K for a system where the $\sim R^{-4}$ behavior largely extends the range of the potential.

The paper is structured as follows. In the next section, we will briefly describe the theoretical methodology, recalling the hyperspherical approach and its recent improvements, and providing details on the considered PES and the calculation of effective potentials. The results from the dynamical calculations will be shown and discussed in section III. Finally, a summary of the work and the conclusions will be given in Section IV.

THEORETICAL METHODS

Not so long ago, errors in ab initio PES were in the order of 1 kcal/mol. Hence it was indeed pointless to attempt an accurate description of the much smaller interactions at LR. Moreover, the high kinetic energies usually considered made possible to assume free-evolution in the dynamics from distances as short as 20-30 a₀. This is a general practice in both time-dependent and time-independent dynamical methods in order to avoid very
long-propagations. However, as we will show, in the unexplored realm of processes at extremely low temperatures, LR interactions cannot be neglected and theoretical tools (used in both electronic structure and nuclear dynamics methodologies) have to be taken to their limit.

**Dynamical methodology**

The hyperspherical quantum reactive scattering method developed by Launay et al. [54] has been widely used and checked in the context of thermal reactive scattering [54]. Already applied to describe ultracold collisions of alkalis [66] [79], the method has proven its capability in reactive processes at very low temperatures, wherein time-dependent techniques (of common use at thermal energies) face insurmountable handicaps. Besides, the particular implementation it uses (in contrast with others involving hyperspherical coordinates), makes it very suitable for systems whose PES shows very deep wells, as it is the case for the title system.

Recent modifications of the method, performed in order to allow the accurate inclusion of small anisotropic LR interactions in the dynamics, were described in depth in ref. [53]. In what follows, we will simply recall the basic concepts, referring to previous works for more details.

In the hyperspherical quantum reactive scattering method, developed by Launay [54], the configuration space is divided into inner and outer regions. The positions of the nuclei in the inner region are described in terms of hyperspherical democratic coordinates. The logarithmic derivative of the wavefunction is propagated outwards on a single adiabatic PES. At a large enough value of the hyper-radius the logarithmic derivative is matched to a set of suitable functions, called asymptotic functions, which provide the collision boundary conditions, to yield the scattering S-matrix. When working at thermal energies, these functions are the familiar regular and irregular radial Bessel functions. They account for the presence of a centrifugal potential without the need of extending the calculation to very large distances, where the centrifugal potential vanishes.

Small albeit important methodological improvements were recently introduced [53] for these functions to account also for anisotropic LR potentials, thus enabling the study of cold and ultracold collisions. These improvements involve the definition of numerical asymptotic radial wavefunctions which are adapted to a specific LR behavior in an analogous way as radial Bessel functions are adapted to the presence of a centrifugal potential. These asymptotic radial functions thus provide the collisional boundary conditions in the presence of general potentials at LR. They are obtained by solving a system of radial differential equations in Jacobi coordinates [53]. Although they imply long propagations from the “asymptotic” region up to the matching hyper-radius (chosen in our case at 35 a.u.) the expense is minimal: the number of coupled equations is reduced to one for $j = 0$. In this way, we can account for the potential at LR while avoiding propagations in hyperspherical coordinates up to extremely large intermolecular separations. Let us note that to converge the elastic cross-sections for the lower partial waves at a collision energy of $10^{-8} \text{K}$, distances on the order of hundreds of thousands of $a_0$ had to be considered. This would be totally unfeasible considering only a propagation in hyperspherical coordinates.

**The electronic energies**

For the $\text{H}^+_2$ system, the only process that can take place below 1.7 eV is the non-charge-transfer proton exchange process, and the reaction can be rigorously described only using the ground adiabatic PES. A deep well ($\approx 4.5$ eV) and a small exoergicity (that of the difference of the zero point energies) are the main features of the PES. A diagram of the minimum energy path and the main energetics of the process is shown in Fig. 1.

New experimental achievements and improvements in the computational performance of electronic calculations call nowadays for more than spectroscopic accuracy, with the aim of building PESs able to describe the whole configuration space (both LR and SR regions) in a balanced way. Such demand is compulsory when studying cold collisions. The PES by Velilla et al. [88], chosen to study the dynamics of the title system, seems to fulfill these requirements. It accurately reproduces the LR interactions, which are included in the functional form of the potential. The asymptotic form of the PES in reactant
Jacobi coordinates \((r,R,\theta)\), is given by:

\[
V_{\text{LR}}(r,R,\theta) = Q_2(r)P_2(\cos \theta)R^{-3} - \frac{1}{\alpha_0} \left[ \frac{1}{3}(\alpha_{\parallel}(r) - \alpha_{\perp}(r))P_2(\cos \theta) \right]R^{-4} + \ldots
\]  

(1)

where \(Q_2(r)\) is the quadrupole moment, and \(\alpha_0(r), \alpha_{\parallel}(r)\) and \(\alpha_{\perp}(r)\) are, respectively, the average, parallel and perpendicular polarizabilities of \(\text{H}_2\). In spite of their dependence on \(r\), their values at the equilibrium distance of \(\text{H}_2\) are \(\sim 0.1\text{ cm}^{-1}\). The range of \(0.1\text{ cm}^{-1}\) is ab initio.

et al. figuration interaction ab initio et al. the surface by Aguado compared with the ones obtained using its "ancestor":

\[
\sim \frac{\alpha_{\perp} - \alpha_{\perp}}{\alpha_{\parallel} - \alpha_{\perp}} \text{ based on the use of a change of variables in LR terms} \ [88], \text{in the configuration space to another might well be less}
\]

and less than \(1\text{ cm}^{-1}\) in the interaction region. The surface implements a recent method, \(\sim \text{ results obtained by using the PES by Velilla fitted using conventional techniques} \ [1]. \text{In order to show the significance of LR effects, the re-}

\[
\text{fit, and it was the difference between the energies given by such an expansion and the}
\]

LR effects and the ab initio energies what was fitted using conventional techniques \([1]\).

In order to show the significance of LR effects, the results obtained by using the PES by Velilla et al. will be compared with the ones obtained using its "ancestor": the surface by Aguado et al. \([2]\). It relies on 8469 configuration interaction ab initio points and a global fit using diatomics-in-molecules approach together with three body corrections. The PES by Velilla et al. is a recent refinement of the PES by Aguado et al. \([2]\), being based on the same set of ab initio points; however it pays especial care in the fitting of the LR region.

The accuracy of the PES, in absolute energies, is in the range of \(0.1\text{ cm}^{-1}\) (0.14 K) in the interaction region and less than \(1\text{ cm}^{-1}\) (1.4 K) in the LR region. However, the error in relative energies (differences) from one point in the configuration space to another might well be less than the tenth of such \([100]\).

### The effective potentials

Let us label with \(\mathbf{l}\) the orbital angular momentum of the atom with respect to the center of mass of the diatom, and with \(\mathbf{j}\) the rotational angular momentum of the latter. The total angular momentum of the nuclei (conserved in an adiabatic approach) is given by \(\mathbf{J} = \mathbf{j} + \mathbf{l}\). A convenient basis in order to expand the nuclear wavefunction in the LR region is the one characterized by quantum numbers \((J, M, v, j, l)\), represented as \(\varphi_{vjl}^{JM}\), with \((v, j)\) the rovibrational quantum numbers of the diatom, \(l\) the relative orbital angular momentum and \((J, M)\) the total angular momentum and its projection on the Space-Fixed (SF) \(Z\) axis. Let us consider the matrix of the electronic potential expressed in this basis, \(\langle \varphi_{vjl}^{JM} | V | \varphi_{v′l′}^{JM} \rangle\). Its diagonal elements are useful in order to understand the dynamics because the diabatic effective potential felt by the colliding partners at a distance \(R\) when approaching in the state \(\varphi_{v0l0}^{JM}\) is given by \(\langle \varphi_{v0l0}^{JM} | V | \varphi_{v′l′}^{JM} \rangle\). Simplifying reasons, we will design with \(\langle V \rangle_{l′,l}(R)\) the matrix element \(\langle \varphi_{vjl}^{JM} | V | \varphi_{v′l′}^{JM} \rangle\).

Regarding the calculation of the potential matrix \(\langle V \rangle_{l′,l}(R)\), it is convenient to calculate first the one associated to another basis, labeled by the projection \(\Omega_j\) of \(\mathbf{J}\) on the Body–Fixed (BF) coordinate system, whose \(z\)-axis is chosen along the reactant Jacobi \(\mathbf{R}\) vector. This BF basis set is given by

\[
\phi_{vjl}^{JM} = \frac{\chi_{v,j}(r)}{r} \sqrt{\frac{2J+1}{4\pi}} D_{\Omega_j}^{JM} \alpha_{\beta,\gamma}(\theta, \phi) Y_J^M(\theta, \phi),
\]

(2)

where \(\chi_{v,j}(r)\) is the radial rovibrational wave function, \(Y_J^M(\theta, \phi)\) the spherical harmonics, and \(D_{\Omega_j}^{JM}\) denotes a Wigner rotation matrix element with \((\alpha, \beta, \gamma)\) being the Euler angles corresponding to the transformation between SF and BF frames. The matrix elements of the PES \(V(R, r, \theta)\) in this basis are given by

\[
\langle V \rangle_{\Omega_j,\Omega_{j′}}(R) = \delta_{\Omega_j,\Omega_{j′}} 2\pi \int_0^\infty \chi_{v,j}^2(r) Y_{\Omega_j}^2(\theta, \phi) V(R, r, \theta) \sin \theta \, dr \, d\theta
\]

(3)

Once the potential matrix is calculated in the BF frame, we change to the SF basis (what involves a combination using \(3j\) symbols) thus obtaining:

\[
\langle V \rangle_{l′,l}(R) = (-1)^{l+l′} \sqrt{2l+1} \sqrt{2l′+1} \sum \Omega_j \left( \frac{j}{\Omega_j} | \begin{array}{c} l \ J \\ 0 \ -\Omega_j \end{array} \right) \left( \frac{j}{\Omega_j} | \begin{array}{c} l′ \ J \\ -\Omega_j \end{array} \right) \langle V \rangle_{\Omega_j,\Omega_{j′}}(R).
\]

(4)
RESULTS AND DISCUSSION

The reaction at low collision energy: the Numerical-Capture Statistical model

The classical Langevin capture model for a potential behaving as $R^{-4}$ is usually applied to rationalize the cross-sections and rate constants corresponding to an ion + neutral collision. Even when the asymptotic expression in Eq. 1 contains a charge-quadrupole term $\sim R^{-3}$, collisions with $j = 0$ correspond to the case $n = 4$ for this reactive system. Indeed, the effective potential which governs the collision behaves as $-C_4/R^4$: the integral $\langle j = 0 | P_2 | j = 0 \rangle$ is null because $| j = 0 \rangle$ is equivalent to the Legendre polynomial $P_0$, and the contribution of the term $\sim R^{-3}$ (as well as the anisotropic polarization term) in Eq. 1 vanishes. Let us remark that, in contrast to neutral + neutral reactions, the $\sim R^{-4}$ behavior extends the range of the interaction to very large distances.

When applied to the title system the Langevin model (used for collisions dominated by attractive potentials and high reaction probabilities) it becomes equivalent to assume that the system is captured in the complex and leads to reaction whenever the collision energy overcomes the centrifugal barrier. In fact, starting from the expression $\sigma(E) = (\pi/k^2)\sum(l+1)P_l(E)$ and: i) calculating the centrifugal barrier height for each $l$ corresponding to an analytical potential $-C_4/R^4$; ii) assuming that $P_l(E)$ is zero below the centrifugal barrier, and the unity over it; and iii) replacing the summation with an integral over impact parameters, one gets the well known Langevin expression for the cross-section $\sigma_L(E) = 2\pi(C_4/E)^{1/2}$ (or $k_L(E) = 2\pi(2C_4/\mu)^{1/2}$ for the rate coefficient, where $k_L(E) = v_{rel}P_0$ and $v_{rel}$ the relative velocity). The value of $C_4$ corresponding to the polarization potential can be easily estimated starting from $\alpha$, the average polarizability of the molecule, and $q$, the charge of the ion, by using the expression $C_4 = q\alpha^2/2$. Taking $\alpha=5.41$ a.u. from the literature [49], we get a value of $C_4=2.70$ a.u. More accurately, one should consider the $C_4$ associated to the PES and calculated from the effective potential corresponding to $J = 0$: as expected, the latter behaves asymptotically as $-C_4/R^4$ with a value for $C_4$ given by 2.71 a0.

The reaction cross-sections for low collision energies obtained using both considered surfaces are shown in Fig. 2. The PES by Aguado et al. seems to be somewhat less reactive than the one by Velilla et al.. In order to understand such difference, we have calculated the effective potentials associated to low partial waves and they are shown in Fig. 3. As can be seen, the centrifugal barriers are lower for the surface by Velilla et al. what explains the higher reactivity. The polarization term, accurately included in the PES, pulls the centrifugal barriers down, thus allowing more incoming flux to reach the inner region and to lead to reaction. Once we have shown the significance of the LR interactions, even at energies well above the cold energy range, we will restrict our calculations to the PES by Velilla et al.

The same values from Fig. 2 are plotted in logarithmic scale in the high energy region of Fig. 3 where the results for much lower collision energies are also shown together with the Langevin predictions. Rate coefficients are shown in Fig. 3 and compared with $k_L(E)$. First of all, let us focus at high collision energies, where many partial waves are open and Langevin model could be valid. Our theoretical cross-sections are found smaller than the Langevin prediction and this is not surprising. Actually, Langevin model is a crude approximation. We can try to improve it in, at least, three ways: i) calculating the heights of the centrifugal barriers numerically, using the effective potentials, thus accounting for deviations from $R^{-4}$ at short-range; ii) performing the summation over partial waves instead of the integral, what will introduce sudden ‘steps’ in $\sigma(E)$; iii) correcting with a statistical factor (6/7 in this case, as discussed here-under) to account for the probability of a complex to decompose into the products arrangement channel. We will call this “improved” Langevin model as ‘numerical-capture statistical model’. The results of the refined model are shown in the high energy region of Figs. 3 and 4. The predicted cross-sections and rates are lower, in better agreement with the calculations. If desired, the steps in the model can be easily suppressed by approximating each centrifugal barrier for an analytical barrier, and using the associated transmission probability instead of the step function.

The factor 6/7 deserves more detailed comments. If the collision is assumed to be mediated by a long-lived complex (due to the deep well in the PES), it is possible to decompose the whole collision process in the step of formation of the collision complex (capture), and the step of its decomposition. Accordingly, the total (summed over
be captured in the complex, $P_i$ terms: i) the probability for the colliding partners to tum numbers ($l_i$iding in the incoming channel $i$), reaction probability, and ii) the probability for, once the complex is formed, decomposing into the product arrangement channel, the ability for, once the complex is formed, decomposing into fragments would be independent of the initial state of the reagents which originated them (except for the total angular momentum and energy conservation). In such extreme case (ergodic hypothesis), we can say that $P_i(E) \approx P_{\text{capt}}(E) \times P_{\text{dec}}(E)$. Furthermore, the fraction of complexes which decompose into the reactants ($B^+ + H_2$) or products ($H^+ + HD$) is roughly proportional to the corresponding number of energetically accessible channels available from the complex, considering all of them as equiprobable. Hereinafter, we will denote the fraction corresponding to products, $P_{\text{dec}}(E)$, as the statistical factor. In particular, if we denote with $A(E)$ and $B(E)$ the number of energetically open channels corresponding, respectively, to the reagent and product arrangements, the statistical factor may be approximated by $B(E)/(A(E) + B(E))$ (number of favored outcomes divided by the total number of equiprobable outcomes). For any $J > 1$ (see note 101) we find that $A(E) = 1$ and $B(E) = 6$, and one gets that $B(E)/(A(E) + B(E)) = 6/7 \approx 86\%$, the statistical factor we have used to correct the Langevin result. However for the particular cases $J = 0$ and $J = 1$ the fractions are different, being $3/4 \approx 75\%$ and $5/6 \approx 83\%$, as corresponds to 3 and 5 open product channels (respectively) versus 1 open reactant channel. Let us note that, if the number of product channels were very big, $B(E) >> A(E)$, then $P_{\text{dec}}(E) \approx 1$ and the result would be equivalent to the Langevin assumption. This quick reasonings can be put in solid grounds by making use of more rigorous statistical models, in their quantum or quasiclassical versions applied in the past to the $H_2^+$ system at thermal energies. They relate the fraction of complexes which decompose into a particular channel to the capture probability of forming the complex starting from it. In our naive reasoning, we are assuming such capture probabilities to be $\approx 1$, what has sense if we are not very close to threshold. We refer to ref. 53 for more details.

In Fig. 7 the comparison of the obtained rate coefficients with the experimental cross-sections multiplied by the relative velocity from Ref. [18] is shown. The agreement is fairly good. Note that the experimental results include also the contribution of ortho-$H_2$. However, the latter should not be very different to the one of para-$H_2$ according to recent calculations.

Finally, it is interesting to note that the Langevin expression $\sigma_L(E)$, which should be valid only for high energies (when many partial waves are open), fulfills the Wigner threshold law ($\sigma_L(E) \sim E^{-1/2}$) in the limit of zero collision energy. Its slope in Fig. 5 thus coincides with the slope corresponding to our results. Such situation only takes place for the $n = 4$ case (ion-induced dipole) and could be considered a happy coincidence (for $n \neq 4$, the collision energy dependence of the cross-section is not any longer $E^{-1/2}$). However, as can be seen in Fig. 5 also the absolute values of both curves (the Langevin cross-sections and our calculated cross-sections) agree remarkably well ($\sigma(E) \approx 1.07\sigma_L(E)$) in the ultracold limit, where only one partial wave is open. This fact deserves an explanation and we will devote the following subsection to rationalize it.

**Low partial waves in the ultracold regime**

When analyzing the ultracold regime for a LR potential behaving as $-C_n/R^n$ ($n > 3$), it is convenient to define a characteristic length, $R_n = (2 \mu C_n/h^2)^{1/(n-2)}$, and a characteristic energy, $E_n = \hbar^2/(2\mu R_n^2)$. The latter is of
the order of the p-wave centrifugal barrier, which appears around \( R_n \). For the case \( n=4 \), \( E_4 \) actually coincides with the height of the centrifugal barrier, assuming that the latter is located far enough for the \(-C_4/R^4\) asymptotic behavior being valid. In our system, \( R_4 \) is approximately 99.7 \( a_0 \) and \( E_4 \approx 8.6 \times 10^{-3} \) K.

The calculations yield the S-matrix as a function of the energy for each total angular momentum \( J \) or, equivalently, for each partial wave \( l \) (for the case \( j = 0 \), both quantum numbers are equal and we will use them interchangeably). This allows the calculation of an energy dependent complex scattering length \( \tilde{a}_{lm}(k) \) in terms of the elastic (diagonal) element of the S-matrix,

\[
\tilde{a}_{lm}(k) = \frac{1}{ik} \frac{1 - S_{lm,lm}(k)}{1 + S_{lm,lm}(k)}
\]

The definition of an energy dependent scattering length is preferable to the use of effective range expansion, which is not useful for very LR potentials like \( R^{-4} \) [40]. Let us denote with \( \alpha_{lm}(k) \) and \( \beta_{lm}(k) \) the real and imaginary part of the complex scattering length: \( \tilde{a}_{lm}(k) = \alpha_{lm}(k) - i\beta_{lm}(k) \). At low enough collision energy they relate to the elastic, \( \sigma_{el} \), and total loss, \( \sigma_{loss} \) (inelastic plus reactive), cross-sections in the following way:

\[
\sigma_{el}^{lm} \to 4\pi(\alpha_{lm}^2 + \beta_{lm}^2) \quad (6)
\]
\[
\sigma_{loss}^{lm} \to 4\pi\beta_{lm}^2 \quad (7)
\]

Given that \( H_2(v=0, j=0) \) is the only rovibrational state of the reactants open at the considered energies, the inelastic process is absent and losses are only associated to reaction, \( \sigma_{loss}^{l} = \sigma_{re}^{l} \). As we are not interested in product-state resolved magnitudes, it is interesting to stress that all the information that will be shown below is contained in the diagonal elements \( S_{lm,lm}(k) \):

\[
\sigma_{el} = \sum_{l,m} \sigma_{el}^{lm} = \frac{\pi}{k^2} \sum_{lm} |1 - S_{lm,lm}(k)|^2 \quad (8)
\]
\[
\sigma_{re} = \sum_{l,m} \sigma_{re}^{lm} = \frac{\pi}{k^2} \sum_{lm} (1 - |S_{lm,lm}(k)|^2) \quad (9)
\]

The behavior of the cross-sections at very low kinetic energies is given by the well known Wigner threshold laws [70, 92], which state that the elastic and the total-loss cross-sections associated to each partial wave vary close to threshold as:

\[
\sigma_{el}^{l} \sim E^{2l} \quad (10)
\]
\[
\sigma_{loss}^{l} \sim E^{l-1/2} \quad (11)
\]

However, threshold laws for elastic scattering are modified for a potential with \( n = 4 \), having a pretty interesting form [70, 92]. The behavior of the phase shift for \( l > 0 \) at very low collision energies is dominated by a term \( \sim E \) originating from the polarization potential [40]. This way, the behavior of the elastic cross-section is given by

\[
\sigma_{el}^{0} \sim \text{constant} \quad (12)
\]
\[
\sigma_{el}^{l} \sim E \quad \text{for } l > 0 \quad (13)
\]

In summary, while the reaction cross-sections are expected to change as \( E^{l-1/2} \), the elastic cross-section will remain constant for \( l = 0 \), while changing as \( \sim E \) for any value of \( l \) bigger than 0. These behaviors can be distinguished in Fig. 3 where the ultracold reaction and elastic cross-sections for the lowest three partial waves are shown. Note the opening of the p-wave (\( J = l = 1 \)) at energies around \( E_4 \). The considered behaviors amount for a total reaction cross-section changing as \( E^{-1/2} \) (and reactive rate coefficient constant) and total elastic cross-section reaching a constant value (elastic rate coefficient changing as \( E^{1/2} \)) in the limit of extremely low kinetic energies, when only \( l = 0 \) is open. Such behaviors can be clearly distinguished in Figs. 5 and 6.

As discussed above for cross-sections, and now switching to rate coefficients, both the Langevin capture model and the Wigner threshold laws predict constant reaction rates for high and low kinetic energies (respectively).
when applied to the title system. The issue is how these constant values relate. From our calculations, the limiting rate at low energies almost coincides with the (classical) Langevin value, the former being 1.07 times the latter (see Fig. [6]). The result is a reaction rate which remains basically constant for a range of more than eight orders of magnitude! Variations would be further smoothed by the Boltzmann averaging and, if confirmed by experiment, an essentially constant thermal rate would result. However the “Langevin behavior” is expected when many partial waves are open. What is then the reason for this “Langevin behavior” when there is only one? What is the reason for this ‘universality’, understood in the sense of an exclusive dependence on the LR interactions (the only ones considered in the capture model)? However paradoxical the situation may appear, collisions at very low kinetic energy favor the LR interactions. The question should probably be the reverse: how is it possible that a capture model, based on LR interactions, is commonly considered in reaction dynamics at high energies? Part of the answer is the following: once we assume that all the flux that reaches the SR region of the PES leads to reaction, we implicitly eliminate any effect that the details of SR region may have on the outcome, and LR is the only thing that remains.

Very recently, quantal versions of the Langevin model have been proposed in two different approaches [15, 39]. Starting from slightly different quantum defect theory frameworks, universal models are obtained which change smoothly from the ultracold to the high energy regime under the same Langevin assumption: all the flux that reaches the short-range (whose amount is controlled by the LR interactions) leads to reaction; or, in other words, the loss probability at SR is the unity. The conclusion derived from these models for the case \( n=4 \) is the following: in the limit of zero kinetic energy, the reactive cross-section should reach a value \( 2\sigma_L(E) \), that is, twice that predicted by the Langevin expression and not simply \( \sigma_L(E) \), which is what we essentially get. As stressed by the authors, such model represents a type of universal behavior which can emerge whenever the number of open channels in a set of coupled channel equations becomes large. However, as already noted, this is not the case for the title reaction, where only 4 channels (three product channels and one reactant channel) are open for \( J=0 \). Luckily, the formalism in Ref. [16] generalizes the model in Ref. [39] to the non-universal regime where the loss probability at SR is less than the unity \( (P^{\text{re}} < 1) \). This model will be applied to our reaction in the following section.
The scattering lengths

In this section, we will apply the quantum model for ultracold reactive collisions in $1/R^6$ potentials, published in ref. [39], to rationalize the results we have obtained in the ultracold regime. The model assumes the formulation of multichannel quantum defect theory (MQDT) by Mies [58, 59] to find a general expression for the complex scattering length $\tilde{a}_{lm}(k)$ as a function of the MQDT functions. This allows to parametrize the dependence of the complex scattering length with $k$ in terms of two real parameters, $y$ and $s$, together with the mean scattering length, $\bar{a}$ [27]. The latter is defined as

$$\bar{a} = \frac{\pi(n - 2)(n-4)/(n-2)}{1^2(1/(n - 2))} R_n$$

where $R_n$ was defined above. In the case $(n = 4) \bar{a}$ coincides with $R_4$ and is thus given by $\bar{a} = (2\mu C_4)^{1/2}/\hbar$ ($\approx 99.7 \ a_0$).

The dimensionless parameter $0 \leq y \leq 1$, the SR interchannel coupling strength, characterizes the SR collision. It relates to $P^\text{re}$, the probability of irreversible loss of flux from the entrance channel due to the dynamics at SR, according to $P^\text{re} = 4y/(1 + y)^2$. The case $y = 1$ corresponds to the Langevin assumption or ‘universal’ case, where all the flux that reaches the SR region leads to reaction.

The dimensionless scattering length $s = a/\bar{a}$ is an entrance channel phase, where $a$ is the “background” $s$-wave scattering length corresponding to the one-channel potential. It is related to the phase of the standing wave due to the interference between the incoming and outgoing waves in the outer region [39, 40]. The limits $s \to \pm \infty$ correspond to a bound state crossing threshold.

The model has been checked already for a few reactive systems [39, 40]. In particular, it has been found able to satisfactorily fit the measured reaction rates for the Penning ionization of Ar by metastable He in a wide range of collision energies over threshold [40], by simply assuming the same values of $s$ and $y$ for all partial waves.

In terms of the parameters of the model, the limit values for the real and imaginary parts of the $s$-wave ($l=0$) complex scattering length are given by [102]:

$$\alpha_{00}(k) \to \bar{a} \frac{s(1 - y^2)}{1 + s^2 y^2}$$
$$\beta_{00}(k) \to \bar{a} \frac{y(1 + s^2)}{1 + s^2 y^2}$$

Regarding $l = 1$, the corresponding predictions are as follows:

$$\alpha_{1m}(k) \to -k\bar{a}^2 \pi/15$$
$$\beta_{1m}(k) \to V k^2 \frac{y(1 + s^2)}{s^2 + y^2}$$

where the characteristic $p$-wave volume for $n=4$ is defined as $V = \bar{a}^3/9$.

With regard to $l=2$,

$$\alpha_{2m}(k) \to -k\bar{a}^2 \pi/105$$
$$\beta_{2m}(k) \to k^4\bar{a}^5 \frac{y(1 + s^2)}{2025(1 + s^2 y^2)}$$

Finally, for $l=3$,

$$\alpha_{3m}(k) \to -k\bar{a}^2 \pi/315$$
$$\beta_{3m}(k) \to k^6\bar{a}^7 \frac{y(1 + s^2)}{2480625(s^2 + y^2)}$$

We have analyzed the scattering lengths obtained from the calculations in terms of these expressions. The upper-left panel of Fig. 8 depicts the real and imaginary parts of the scattering length corresponding to $J = 0$ (obtained using the element $S_{lm,l'm'} = S_{00,00}$ from our calculations) as a function of the collision energy. Both reach constant values in the ultracold regime, in agreement with the Wigner threshold laws discussed in the previous subsection and with the fact that Eq. (15) and Eq. (15) are independent on $k$. The real and imaginary parts of the scattering lengths corresponding to the three following partial waves, $J = 1, J = 2$ and $J = 3$ are also shown in the other three panels of the Fig. 8. The limiting behaviors as a function of the energy are again in perfect agreement with the expected threshold laws and the power of the dependence on $k$ of the expressions (15)-(22).

In order to parametrize our results in terms of $s$ and $y$, let us consider first the case $l = 0 (J = 0)$. Introducing the limiting values we have obtained in the lhs of Eq. (15) and Eq. (16) and solving for the parameters $y$ and $s$, we obtain $y_{l=0} = 0.34$ ($P^\text{re} = 77\% \approx 3/4$) and $s_{l=0} = -0.8$. The parametrization for higher values of $l (J)$ is not so simple and we will consider real and imaginary parts separately. Wigner threshold laws are already modified starting from $l = 1$. The term that dominates the behavior of $\alpha_{lm}(k)$ for $l > 0$ does not depend on $y$ or $s$, and the real parts, given by Eqs. (17), (19) and (21), can be compared directly with our scattering results. The values for $\alpha$ in the three considered cases agree very well (within 1%) with those given by the expressions (17), (19) and (21). This coincidence can be considered a test of the theory and serves to ensure the convergence of the (computationally demanding) scattering calculations. It should be remarked that these expressions do not depend on $s$ or $y$, and hence we can consider them as really universal, being only dependent on the $C_4$ and thus of the LR part of the potential exclusively.

The analysis of the imaginary parts given by Eqs. (18), (20), and (22) is not so straightforward. Given that the real part of the scattering length, $\alpha_{lm}(k)$, does not depend on $s(l)$ and $y(l)$, it is not possible to solve for the two unknown quantities only using the expression of $\beta_{lm}(k)$. Similarly to the procedure followed in
what can be done instead is to assume that \( y \) and \( s \) do not strongly depend on \( l \) and check if the values for \( \beta_{lm} \), obtained by substituting \( y(l = 0) \) and \( s(l = 0) \) in Eqs. \([18, 20, 22]\) are not very different from those obtained in the scattering calculations. After doing that, we find that the ratios of the \( \beta_{lm} \)'s we obtain substituting \( y(l = 0) \) and \( s(l = 0) \) in the expressions of the model, and the accurate ones, extracted from our scattering calculations, are: 0.4 for \( J = 1 \), 1.4 for \( J = 2 \) and 0.7 for \( J = 3 \). Therefore, the agreement seems to be acceptable on average. This is likely one of the reasons that the assumption of the same values of \( s \) and \( y \) for different partial waves was found to work well for the Penning ionization of Ar by metastable He. In such a system the reduced mass is bigger (four times) than in present case, what increases the number of partial waves considered, and hence probably reducing the average error of such strong approximation. A necessary condition (but not sufficient) for the same values of \( s(l = 0) \) and \( y(l = 0) \) to be valid for other partial waves is that the (\( n = 4 \)) behavior in the potential extends from the asymptote down to the region where the corresponding centrifugal barriers are located. This condition is fulfilled in this case for the considered partial waves whose centrifugal barriers lie around 99 \( a_0 \), 57 \( a_0 \), and 41 \( a_0 \), respectively. In this way, the expressions of the model could, in principle, work well with values for the parameters that do not strongly depend on \( l \). However, it is interesting to note that the small number of states which are coupled to the incident channel changes when moving from \( J = 0 \) to higher values of \( J \), as explained above. This way, differences in the parameters, in particular in \( P^{re} \) and thus in \( y \), are not unexpected.

To the best of our knowledge, the values for \( y \) (\( P^{re} \)) and \( s \) in the considered model are considered phenomenological. To date they have been obtained for very particular systems by fitting experimental results to the analytical expressions of the model \([10]\) (equivalent to what we have done with our theoretical results to extract \( s \) and \( y \)). However, we have some clues to rationalize the value for \( y(l = 0) \) that we have finally found; in fact, our previous expectations where confirmed with such value. The so-called universal case (\( y = 1 \)), usually considered as a first approach to any system in recent literature, may be characterized for a number of coupled states which is so large that one may assume that all the reactive flux is irreversibly lost from the incident channel. However, even if the number of coupled channels inside the well is very large for the title system, its exothermicity is low (the difference in zero point energies) and consequently, the number of open rovibrational states is small (three for the HD product and \( J = 0 \)) and hence the number of open channels coupled to the incident is also small. This anticipates the possibility, discussed above, of a significant flux returning from the complex (recrossing) to the incident channel. According to this, it would be possible to relate the value obtained for \( P^{re} \) with the statistical factor \( 3/4 \) corresponding to \( J = 0 \). If the randomization and lost of memory of the system at SR (in the complex) were complete, a \( P^{re} = 3/4 \), as obtained, would be reasonable. A value of \( s = -0.8 \), very close to -1, would guarantee that resonant states close to threshold were not masking the equiprobable distribution among states that, on average, the presumably long residence time within the well would imply.

However, the situation is not so simple. The very good agreement between the statistical factor and \( P^{re} \) might simply be fortuitous. Actually, it is difficult to derive an unambiguous proportionality between \( P^{re} \) and the statistical factor. Calculations with \( J = 0 \) where the mass of the deuterium is artificially modified in order to change the number of open rovibrational states of HD (thus modifying \( B(E)/(A(E) + B(E)) \)), give rise to a value of \( P^{re} \) which keeps some correlation with the corresponding statistical factor. However this value can also widely oscillate, and the oscillations are usually found in coincidence with bigger values of \( s \), which can be associated to resonances. Actually, as we will discuss hereunder, it is expected that the local effect of resonances can modify the average behavior expressed by the statistical factor.

More work has to be performed to conclude the average agreement between the values of \( P^{re} \) and statistical factors in systems with a well. However, let us note that we are considering a real system which only approximately fulfills all the assumptions in the model. We are using expressions \([15, 17] \) presumably only valid for the HD product and

![FIG. 8: Real and imaginary parts of the scattering lengths obtained in the calculations for the 4 lowest partial waves. The scale is logarithmic and the absolute value of \( \alpha \), which is mostly negative, is plotted. The values for \( J = 1, 2 \) and \( 3 \) (in continuous line) are compared with the predictions from the model in Ref. \([10] \) (in dashed lines), calculated using Eqs. \([17-22] \), assuming for \( s \) and \( y \) the same values that have been obtained for \( J = 0 \).]
for an ideal case, to extract particular values of parameters whose meaning is only defined in that ideal case. It is difficult to predict how this divergence from ideality is going to affect not only the value for \( s \) and \( y \) but also their meaning. The pure roles of \( y \) and \( s \) are probably difficult to unravel for real systems.

For the title reaction, statistical models seem to yield results in good agreement with accurate, fully converged quantum scattering for thermal reactions rates even at low temperatures [26]. As an instance, in Fig. 1 of ref. [26] it is shown that the statistical model by Rackham and Manolopoulos [67] leads to a step-like reaction probability that on average reproduces the highly structured one found in the quantum calculations. Since for thermal rate coefficients only the average value over a range of energies matter, the statistical model has proved to render accurate rate coefficient values. However, it remains to be seen if these models can work in the ultracold regime where a coarse grid hypothesis is not longer valid. Moreover, by its nature, the statistical models would fail to describe the detailed effect of resonances, which are ubiquitous as long as it exists a sufficiently deep well. Given the resonant nature of the behavior close to threshold, the statistical model may find unsurmountable obstacles in the cold and ultracold regimes. Implicit in the statistical model is the assumption of a lost of coherence between external and internal regions of the potential; the presence of a resonance, which means an increase of amplitude in the inner region, would invalidate such an assumption preventing the factorization \( P_r^i(E) \approx P_{\text{capt}}^i(E) \times P_{\text{prod}}^i(E) \) that was discussed above.

In this regard, the structure of the previous expression is similar to the ansatz \( P_r^i(E) \approx P_{\text{LR}}(E) \times P_{\text{SR}}(E) \), which is at the conceptual basis of some approximate approaches to ultracold reactions recently proposed [45]. This ansatz is inspired by the MQDT concept of factoring the S-matrix into separate parts due to the short and LR interactions. Accordingly, the flux which reacts is only the fraction \( P_{\text{SR}}(E) \) (determined by the couplings at SR) of the total transmitted by the LR interactions, \( P_{\text{LR}}(E) \). This seemingly naive approach can be put into question by the non-local nature of the wave function, especially when resonant states lie close to threshold. This can be concluded from the results of other models [44, 46, 50] and, in particular, by using Eq. (16). From this equation and applying expression (6), it can be seen that the reaction probability at ultracold energies is given by

\[
P_r^i(E) = 4k\tilde{\alpha} \times \frac{2y}{1 + y^2} \quad (24)
\]

The second term can be paradoxically bigger that 1 for low values of \( y \) and big values of \( s \) (that is, for resonant states close to threshold), so it cannot be associated in general to a probability. For the particular case of unit loss probability at short range, one gets \( P_r^i(E) = 4k\tilde{\alpha} \times 1 \), what is consistent with the ansatz and with the intuitive, but wrong, conclusion that the reaction probability is limited by the amount of probability that the LR is able to capture. Also for the case \( s = 1 \) (which can be associated with minimum influence of resonant states), the expression given by the model

\[
P_r^i(E) = 4k\tilde{\alpha} \times \frac{4y}{(1 + y^2)^2} \quad (25)
\]

but only for \( y \approx 1 \) [104]; for a general value of \( y \), differences between both expressions can be as big as 25\%. However, for general large values of \( s \) and small values of \( y \) the factor \( y(1 + s^2)/(1 + s^2y^2) \) can be bigger than one, leading to reaction probabilities which are bigger than the capture; it is thus difficult to conceive how a statistical factor could account for it. We have checked this extreme case again by artificially changing the mass of the deuterium. For some particular values of the mass, the reaction probability is found much bigger than the capture by the potential in the reactant channel, \( 4k\tilde{\alpha} \). This is found, for example, for a value of \( s = -3.98 \). Let us finally note that the statistical model, in the way that it is usually implemented, calculates the capture probability of a particular state considering its coupling with other states in the entrance channel [67], thus providing a dynamical value for the capture which may be different than the one-channel capture \( P_r^i(E) = 4k\tilde{\alpha} \). However, this reasoning calls our attention to possible limits for applicability of the statistical model to very low temperatures or kinetic energies in the presence of resonant states close to threshold.

**SUMMARY AND CONCLUSIONS**

We have carried out a detailed study of the \( \text{D}^+ + \text{H}_2 \) ion-molecule system under the cold and ultracold regimes, covering the \( 10^{-8}–150 \) K collision energy range. Rigorous fully converged quantum mechanical calculations have been performed on the potential energy surface by Velilla et. al, which faithfully reproduces the long range (quadrupole and charge-induce dipole) behavior. The quantum dynamical methodology used in this work is especially appropriate to calculate \( \text{ab initio} \) cross sections at extremely low collision energies. In addition, the method is ideally suited to tackle complex mediated reactions.
The methodology has been applied for the first time to a reactive ion-molecule system governed by a $R^{-4}$ potential at long range. This makes the calculations more demanding since propagations up to distances on the order of $10^5 \, a_0$ are required. The calculated elastic and reactive cross sections and rate coefficients have been found to comply with the expected threshold laws. Interestingly, the behavior in the ultracold regime is well described by the classical Langevin model, which is expect to work only when many partial waves are open. Should this behavior be confirmed by the experiment, it would have been found a system with a reaction rate coefficient which remains almost constant in a kinetic energy range of more than ten orders of magnitude.

The detailed calculated reaction probabilities and the associated scattering lengths have allowed us to test the quantum defect theory model by Jachymsky et al. for various partial waves. The assumption made in previous calculations. The scattering lengths calculated under this specific partial wave has been assessed with the present calculations. The scattering lengths calculated under this assumption are found in acceptable, at least on average, agreement with the scattering results.

In addition, rough statistical assumptions have been found able to rationalize the obtained loss probability at short range. Although there seems to be a correlation between the statistical factor (corresponding to the statistical model) and the loss probability at short range (corresponding to the model by Jachymsky et al.) in the case of this process, mediated by a deep well, more work is needed to fully evaluate it.

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Let us consider, for example, the case $J = 2$. According to Fig. 1, there are three open rovibrational states of HD at the considered collision energies. The incoming channel has quantum numbers ($v=0$, $j=0$, $l=2$, $J=2$), and the total angular momentum, $J = 2$, and the parity, $\epsilon = (-1)^{j+l} = +1$ are conserved in the collision; therefore, the product collision channels which are coupled to the incoming channel are ($v'=0$, $j'=0$, $l'=2$, $J=2$), ($v'=0$, $j'=1$, $l'=3$, $J=2$), ($v'=0$, $j'=1$, $l'=1$, $J=2$), ($v'=0$, $j'=2$, $l'=4$, $J=2$), ($v'=0$, $j'=2$, $l'=2$, $J=2$), ($v'=0$, $j'=2$, $l'=0$, $J=2$). This way, there are 7 coupled channels, with $A(E) = 1$ and $B(E) = 6$.

Equations (15), (16), (17), (18) were kindly provided by the authors of ref. [46]; Equations (19), (20), (21), (22), were deduced by the authors of this work following the formalism in ref. [46], and according to the information in ref. [40].

This capture probabilities can be numerically calculated for any value of $k$ by propagating inwards the logarithmic derivatives of regular and irregular Bessel functions under the effect of the LR potential and matching at short distance with perfect absorption WKB conditions. The value of these capture probabilities at very low $k$ is given by $4k\bar{a}$.

This can be seen assuming $y = 1 - x$ and expanding in powers of $x$ for $x << 1$.