Near-resonant effects in the quantum dynamics of the H+H₂ → H₂ + H⁺ charge transfer reaction and isotopic variants

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The non-adiabatic quantum dynamics of the H+H₂ → H₂ + H⁺ charge transfer reactions, and some isotopic variants, is studied with an accurate wave packet method. A recently developed 3×3 diabatic potential model is used, which is based on very accurate ab initio calculations and includes the long-range interactions for ground and excited states. It is found that for initial H₂^+(v=0), the quasi-degenerate H₂(v’=4) non-reactive charge transfer product is enhanced, producing an increase of the reaction probability and cross section. It becomes the dominant channel from collision energies above 0.2 eV, producing a ratio, between v’=4 and the rest of v’s, that increases up to 1 eV. H+H₂^+ → H₂^+ + H exchange reaction channel is nearly negligible, while the reactive and non-reactive charge transfer reaction channels are of the same order, except that corresponding to H₂(v’=4), and the two charge transfer processes compete below 0.2 eV. This enhancement is expected to play an important vibrational and isotopic effect that need to be evaluated. For the three proton case, the problem of the permutation symmetry is discussed when using reactant Jacobi coordinates.

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I. INTRODUCTION

Hydrogen is the most abundant element in Universe, with nearly 73% of the baryonic mass, and plays a fundamental role in the chemistry of the interstellar medium (ISM). It is at the origin of the chemical cycles of most of the molecules, which in turn play a fundamental role in the collapse of molecular clouds to form stars and planetary systems. The most abundant molecular species are H₂ and H₂^+, while H₂^+, formed by ionization of H₂ by cosmic rays, is rapidly destroyed by the exothermic reaction

\[ \text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H}. \] (1)

H₂^+ is considered as the universal protonator by producing hydrides when colliding with atoms and molecules. Its collisions with H₂ produce ortho/para transitions of the two species, and/or to its deuteration when colliding with HD isotopic variant.

In local galaxies, the formation of H₂ is attributed to reactions on cosmic grains and ices because the gas phase routes have too low rate constants to reproduce the observed abundances. In Early Universe, where grains and ices do not exist, one of the key problems is therefore to determine the processes, and their related rate constants, giving rise to H₂. One of this is the charge transfer reaction

\[ \text{H} + \text{H}_2^+ \rightarrow \text{H}_2 + \text{H}^+, \] (2)

where the reactant and product channels of Eq. 2 correspond to the first excited and the ground electronic states of the H₂^+ system, respectively.

H₂^+ plays a fundamental role in astrochemistry and it has been the subject of many studies summarized in review. Its infrared spectrum was first detected in the laboratory by Okl and later in the space. Since then, H₂^+ has become commonly used to probe spacial conditions, such as a thermometer and a clock of cold molecular clouds. Its infrared spectrum has been theoretically characterized with spectroscopic accuracy based on highly accurate potential energy surfaces (PESs), local and global studies.

The H^+ + H₂ exchange reaction has been the subject of many experimental and theoretical studies. This reaction governs the ortho/para transitions of H₂ and is also responsible of the H₂ deuteration. For energies below ≈ 1.82 eV, this reaction takes place in the ground singlet state of H₂^+. In the ground H₂^+ electronic state there is a deep insertion well, of ≈ 4.6 eV, and the dynamics is mediated by a dense manifold of resonances, and exact calculations show that the reaction proceeds through a statistical mechanism. Above 1.82 eV collision energy, the H₂^+ + H channel becomes accessible, opening the charge transfer process, inverse to the reaction 2, and has been studied in a broad energy range. Furthermore, the non-adiabatic transitions in H₂^+ were studied recently in photodissociation experiments by Urbain et al.

In spite of all these studies on H₂^+, reaction 2 has only been studied experimentally by Karpas et al. by McCartney et al. at energies of 30-100 keV, and more recently Andrianarijona et al. studied the H + D₂^+ isotopic variant in a broader energy range of 0.1-100 eV. The experimental study of reaction 2 have the difficulty of involving two radical reactants, and accurate theoretical simulations are then of high interest to provide realistic rate constants for the model of Early Universe. Some approximated theoretical treatments where applied to reaction 2 during the publication of this work. In this work we present accurate quantum wave packet calculations of the H+H₂^+ charge transfer (CT) reaction, and some isotopic vari-
nants, at collision energies below 1 eV using a very accurate set of three coupled PESs recently proposed\textsuperscript{74} which include long range interactions for the ground and excited electronic states. The manuscript is distributed as follows. First, in section 2, a brief description of the PESs and dynamical methods are shown, presenting a description of the permutation symmetry problem. In section 3 the theoretical simulations are shown and discussed, and, finally, section 4 is devoted to extract some conclusions, outlining future work.

II. METHODOLOGY

A. Diabatic electronic representation

The potential used is described by a $3 \times 3$ diabatic matrix, each diagonal element corresponding to a positive charge in each of the nuclei\textsuperscript{74}. It consists of a zero-order diatomics-in-molecules (DIM) matrix\textsuperscript{75} describing accurately the H$_2$ and H$_2^+$ diatomic fragments (shown in Fig. 1), plus three-body terms added in the diagonal, and non-diagonal matrix, $V^{3B}$, as it was proposed by Varandas and co-workers\textsuperscript{76}. In this potential the long range term has been improved\textsuperscript{23} and included in all the electronic states. The dominant long range terms for H+H$_2$ are the charge-induce dipole and charge-induced quadrupole dispersion interactions, varying as $R^{-4}$ and $R^{-6}$, respectively. For H$^+$+H$_2$ the dominant long range terms are the charge-quadruopol and the charge-induced dipole dispersion energies, varying as $R^{-3}$ and $R^{-4}$, respectively. The $V^{3B}$ was fitted to very accurate ab initio calculations using multi-reference configuration interaction (MRCI) calculations, performed with the MOLPRO suite of programs\textsuperscript{77}. A complete basis set (CBS) approximation was done based on the aV5Z and aV6Z basis sets of Dunning\textsuperscript{78}. These $V^{3B}$ matrix elements change gradually what allows a very accurate fitting, with a small root mean square error\textsuperscript{24}, what is an advantage as compared to the fitting of the sharply varying non-adiabatic matrix elements (NACMEs) required when using an adiabatic representation\textsuperscript{55}.

Diabatic representations are generally considered to be approximate, due to the impossibility to eliminate all NACMEs as a function of all internal coordinates because of the curl condition\textsuperscript{79,80}. The quasi-diabatic representation of the PES used here\textsuperscript{24} is considered as a regularization representation\textsuperscript{80,81} in which the singularities present at conical intersections (CI) are removed exactly\textsuperscript{81}. In the vicinity of CIs the calculation of NACMEs presents numerical problems what adds some error in the adiabatic representation since the Born-Oppenheimer is ill-conditioned at CIs\textsuperscript{82}. The resulting NACMEs obtained by Aguado et al.\textsuperscript{24} showed to be in excellent agreement with the ab initio points. Moreover, the residual NACMEs appearing in all diabatic representation are very small in the present case, because the three-fold basis is rather complete in this system. These residual NACMEs are very small, and only appreciable far from CIs, where the energy difference among the different electronic states is so large that they can be neglected without loss of accuracy.

FIG. 1. Potential energy curves and vibrational levels of H$_2$ (D$_2$) and H$_2^+$ (D$_2^+$). The radial part of the nuclear wave functions for H$_2^+$ (D$_2^+$) have been represented in green.

Quasi-diabatic representations are not unique. In Ref.\textsuperscript{74} it was considered a minimum basis set formed by 3 functions, denoted $\phi_i$, in which there is a positive charge of nucleus $i$, and one 1s electron in the remaining nuclei. In this basis set, the excited $\text{H}_2$ ($^{2}\Sigma_u^+$) is a linear combination of at least two $\phi_i$ functions. A unitary transformation is done, in order to define properly the $\text{H}_2$ ($^{4}\Sigma_u^+$) and $\text{H}_2^+$ ($^{3}\Sigma_u^-$, $^{2}\Sigma_u^+$) for a particular (reactant) rearrangement channel, as

\begin{equation}
\phi^1_1 = \phi_1 \\
\phi^1_2 = \frac{1}{\sqrt{2}} (\phi_2 - \phi_3) \\
\phi^1_3 = \frac{1}{\sqrt{2}} (\phi_2 + \phi_3).
\end{equation}

Transforming the $3 \times 3$ potential accordingly, the H$_2$ and H$_2^+$ ground electronic states become diagonal in channel 1, corresponding to the hydrogen 1 at very long distances from the other two, and the corresponding potentials are shown in Fig. 1. However, on the other two rearrangements, the potential matrix is non-diagonal, and the diabatic couplings are non-zero as can be seen in the right panels of Fig. 1 where they are represented in Jacobi coordinates, $r$ and $R$ for a collinear configuration. As a consequence, the rovibrational states of the products are expanded in several electronic states, for H$_2$ and H$_2^+$ as

\begin{equation}
\phi^{i=2,3}_{ij}(r') = \sum_k \phi^1_k C^{i,j}_{k}(r')
\end{equation}

\begin{equation}
\phi^{i=2,3+}_{ij}(r') = \sum_k \phi^1_k C^{i,j+}_{k}(r'),
\end{equation}

\begin{align}
\phi^1_1 &= \phi_1 \\
\phi^1_2 &= \frac{1}{\sqrt{2}} (\phi_2 - \phi_3) \\
\phi^1_3 &= \frac{1}{\sqrt{2}} (\phi_2 + \phi_3).
\end{align}
respectively, where \( r' \) denotes the internuclear distance in the corresponding product Jacobi coordinates \( r' = r_{13} \) or \( r' = r_{12} \) for \( i = 2 \) and \( 3 \), respectively.

The diagonal and non-diagonal elements of the potential matrix in this diabatic representation are shown in Fig. 2 for a collinear configuration. For long \( R \) and short \( r \) values, the diagonal terms represent \( \mathrm{H}_2(1\Sigma^+_g) \) (bottom left panel), the \( \mathrm{H}_2^+(2\Sigma^+_u) \) (middle left panel) and \( \mathrm{H}_2^+(2\Sigma^+_u) \) (top left panel), the last being purely repulsive. The diagonal terms at long \( r \) and \( R \) values are repulsive, and do not represent the products channels because the non-diagonal terms (shown in the right panels) are non-zero and pretty large. In the reactant channels (long \( R \) and short \( r \) values) the \( \langle 1 | V | 2 \rangle \) non-diagonal coupling term, coupling \( \mathrm{H}_2^+ (2\Sigma^+_u) \) with \( \mathrm{H}_2(1\Sigma^+_g) \), decrease slowly with increasing \( R \), being of the order of \( \approx 1 \) meV at \( R=7 \) Å. This clearly shows that this charge transfer coupling extends towards very long \( R \) distances.

B. Quantum wave packet calculations

The reaction dynamics of the H/D collisions with \( \mathrm{H}_2^+(v=0,j=0) \) and \( \mathrm{H} \) with \( \mathrm{D}_2^+(v=0,j=0) \) are studied here using a quantum wave packet method as implemented in the MADWAVE3 program.\(^{29,30,66}\) For each total angular momentum, \( J \), the state-to-state \( S \)-matrix elements are calculated using a reactant Jacobi coordinate based method,\(^{22}\) generalized to consider product rovibrational states expanded in several electronic states, as in Eq. 4. Three different processes (\( \alpha \) channels) are distinguished

\[
\mathrm{A} + \mathrm{B}_2^+ (v = 0, j = 0) \rightarrow \mathrm{A}^+ + \mathrm{B}_2(v', j') \\
\rightarrow \mathrm{AB}^+(v', j') + \mathrm{B} \\
\rightarrow \mathrm{AB}(v', j') + \mathrm{B}^+ 
\]

with \( \mathrm{A} = \mathrm{H} \), \( \mathrm{D} \) and \( \mathrm{B}_2 = \mathrm{H}_2 \), \( \mathrm{D}_2 \). Channels \( \alpha = 1 \) (NRCT) and 3 (RCT) correspond to products in the ground adiabatic states, either in the reactants or products channels, respectively. Channel \( \alpha = 2 \) (ER) corresponds to exchange products in the first excited adiabatic state.

![FIG. 2. Contour plots of the diagonal (left panels) and non-diagonal (right panels) elements of the 3×3 potential matrix at a Jacobi angle of 0°, as a function of the Jacobi distances \( r \) and \( R \), in the diabatic representation of functions \( \phi_j^\dagger \). In the diagonal terms, the zero of energy is set at the eigen value of \( \mathrm{H}_2^+ (v = 0, j = 0) \) ground rovibrational state, which is at 2.09 eV in Fig. 1. The absolute value of nondiagonal terms are plotted in logarithmic scale.](image)

The parameters used in the wave packet calculations are listed in table 1. Briefly, the initial wave packet corresponds to the product of the \( \mathrm{H}_2^+ (v=0,j=0) \) ro-vibrational eigenfunction, a normalized Wigner function for \( J \) and a real Gaussian function, describing the translation on the \( \mathrm{R} \) Jacobi distance (between the incoming \( \mathrm{A} \) atom and the center of mass of \( \mathrm{H}_2^+ \)), initially placed at \( R_0 \), with a central energy \( E_0 \) and an energy width \( \Delta E \). The flux on individual rovibrational states are analysed at \( R_\infty \) and \( R_\mathrm{abs} \) for reactants and products, respectively. The wave packet is absorbed at the edges of the radial grid by multiplying it by an absorbing function \( \rho^{n} \) for \( \rho \geq \rho_{\text{abs}} \) (\( \rho = r \) or \( R \)) at each Chebyshev iteration, using a modified Chebyshev propagator.\(^{23} \) Using this propagator only a real wave packet is propagated and the corresponding kinetic term is evaluated using a sine Fourier transform which ensures the proper regular behaviour at \( R = 0 \) appearing in this reaction. Finally, a Gauss-Legendre quadrature is used to describe the Jacobi angle \( \cos \gamma = r \cdot R/rR \), and

TABLE I. Parameters used in the wave packet calculations in reactant Jacobi coordinates: \( r_{\min} \leq r \leq r_{\max} \) is the \( \mathrm{H}_2 \) internuclear distance, \( R_{\min} \leq R \leq R_{\max} \) is the distance between \( \mathrm{H}_2 \) center-of-mass and the \( \mathrm{A} \) atom, \( 0 \leq \gamma \leq \pi \) is the angle between \( r \) and \( R \) vectors.

| Parameter | Units | Value |
|-----------|-------|-------|
| \( r_{\min} \) | Å | 0.1 |
| \( r_{\max} \) | Å | 20 |
| \( r_{abs} \) | Å | 16 |
| \( R_{\min} \) | Å | 16 |
| \( R_{\max} \) | Å | 20 |
| \( R_{abs} \) | Å | 16 |
| \( E_0 \) | eV | 0.5 |
| \( \Delta E \) | eV | 0.5 |
| \( R_\infty \) | Å | 10 |
| \( R_\mathrm{abs} \) | Å | 20 |

The parameters used in the wave-packet calculations are listed in table 4. Briefly, the initial wave packet corresponds to the product of the \( \mathrm{H}_2^+ (v=0,j=0) \) ro-vibrational eigenfunction, a normalized Wigner function for \( J \) and a real Gaussian function, describing the translation on the \( \mathrm{R} \) Jacobi distance (between the incoming \( \mathrm{A} \) atom and the center of mass of \( \mathrm{H}_2^+ \)), initially placed at \( R_0 \), with a central energy \( E_0 \) and an energy width \( \Delta E \). The flux on individual rovibrational states are analysed at \( R_\infty \) and \( R_\mathrm{abs} \) for reactants and products, respectively. The wave packet is absorbed at the edges of the radial grid by multiplying it by an absorbing function \( \rho^{n} \) for \( \rho \geq \rho_{\text{abs}} \) (\( \rho = r \) or \( R \)) at each Chebyshev iteration, using a modified Chebyshev propagator.\(^{23} \) Using this propagator only a real wave packet is propagated and the corresponding kinetic term is evaluated using a sine Fourier transform which ensures the proper regular behaviour at \( R = 0 \) appearing in this reaction. Finally, a Gauss-Legendre quadrature is used to describe the Jacobi angle \( \cos \gamma = r \cdot R/rR \), and
the corresponding kinetic terms are evaluated using a Discrete Variable Representation (DVR) method. For \( J=0 \), about \( 8 \times 10^6 \) iterations are needed to converge the reactions probability down to 0.01 eV. This long propagation is needed because of the presence of resonant structures that will be commented below. This is also the situation of higher \( J \) until the rotational barrier push the reactive and NRCT probabilities towards higher energy, what happens at \( J=14 \) and 17 for H/D + H\(_2\) cases, respectively. For higher \( J \)'s, the number of iterations needed gradually decreases.

The calculations have been performed for all \( J \) up to \( J=15 \) and \( J=20 \) for \( A=\) H and D, respectively. For higher values of \( J \), wave packet calculations are performed every 5 \( J \) values up to \( J=60 \) and \( J=80 \), for \( A=\) H/D, respectively. A maximum of helicity components \( \Omega_{\max}=23 \) is considered in the \( J>0 \) calculations. For intermediate \( J \) values, where no wave packet calculations were done, an interpolation method based on the \( J \)-shifting approximation is performed to evaluate the individual state-to-state \( \Sigma^2 \) matrix elements.

The state-to-state integral cross sections are then evaluated using the usual partial wave expansion as

\[
\sigma_{ij\rightarrow i'j'}(E) = \frac{\pi k^2}{(2J+1)} \sum_{J\Omega'\ell'}(2J+1) \left| S_{ijJ\Omega\rightarrow i'j'\Omega'}(E) \right|^2
\]

(6)

C. Symmetry considerations

Dealing with two (D+H\(_2\)\(_+\)) or three (H+H\(_2\)\(_+\)) hydrogen atoms, fermions with nuclear spin \( i=1/2 \), some considerations about the permutation symmetry should be done. The total wave function has to be antisymmetric under the exchange of any hydrogen pair. The total wave function can be factorized as a product of electronic, nuclear spin and rovibrational components as \( \Psi = \Psi_e \Psi_s \Psi_{rot} \). The symmetry of the electronic function, \( \Psi_e \), is analyzed in the body fixed frame of the nuclei, and the permutation of any pair of nuclei corresponds to a reflection through a plane perpendicular to the molecular plane in\( _1 \). In this case, all singlet states of H\(_2\)\(_+\) are totally symmetric. The nuclear spin functions, \( \Psi_s \), are characterized by the total nuclear spin, \( I_2 \) and \( I_3 \), for 2 and 3 hydrogen systems, respectively. \( J=0 \) and 1, and the corresponding functions \( \Psi_{sJ} \) are antisymmetric and symmetric with respect to the permutation of the two hydrogen atoms, respectively. To make the total wave function antisymmetric, the corresponding rovibrational function have to be symmetric and antisymmetric for \( I_2=0 \) and 1, respectively. In diatomic molecules, this corresponds to the usual separation between even and odd rotational levels, since the symmetry of spherical harmonics is \((-1)^j\), denoted as para and ortho, respectively.

For three hydrogen atoms system, \( I_2=1/2 \) and 3/2, and the spin functions can be written as \( |I_3M_3;I_2\rangle = \sum_{m_2} (i_2,1/2|m_2,\sigma, I_3,M_3)|1/2, \sigma \rangle |i_2,m_2\rangle \), where \( |i_2,m_2\rangle \) is the spin function of two hydrogen, each one described by \( |1/2, \sigma \rangle \), and \( (\rangle \) are Clebsch-Gordan coefficients. The existing functions are then \( |3/2M_3;1\rangle, |1/2M_3;1\rangle \) and \( |1/2M_3;0\rangle \), with \( I_2=3/2, 1/2 \) and 1/2, respectively. Considering the \( D_{3h} \) permutation-inversion group, the spin functions with \( I_3=3/2 \) (ortho) belong to the \( A_1 \) representation, while with \( I_3=1/2 \) (para) belong to the \( E \) representation. To build antisymmetric total wave functions, the corresponding rovibrational components have to belong to \( A_2 \) (for \( I_2=3/2, \) ortho) and \( E \) (for \( I_2=1/2, \) para) representations. It should be noted here, that the product for \( I_2=1/2 \), the total symmetry is \( E \times E = A_1 + A_2 + E \), and only \( A_2 \) is anti-symmetric while the other solutions are not physically allowed.

All this said, and neglecting the weak hyperfine nuclear spin rotation coupling, the spin of each hydrogen atom is conserved, and therefore the transformation from ortho to para, and viceversa, can only take place by hydrogen exchange, i.e., by a reaction.

When using reactant Jacobi coordinates, the permutation symmetry of the D+H\(_2\)\(_+\) and H + D\(_2\)\(_+\) is fully account for, while this is not the case for H+H\(_2\)\(_+\). In the three identical hydrogen atoms case, the \( A_2 \) and \( E \) representation has to be considered, separately, while the \( A_1 \) does not exist. Thus, the diatomic rotational channels (for reactants and products) included in each representation of the nuclear wave function are:

\[ E : \text{even and odd } j,j' \rightarrow I_1=1/2, I_2=1,0 \text{ (para) of } A_1 \]
\[ A_1 : \text{only even } j,j' \rightarrow I_1=1/2 \text{ does not exist for } i=1/2 \]
\[ A_2 : \text{only odd } j,j' \rightarrow I_1=3/2 \text{ (ortho) of } A_1. \]

Clearly the case of three identical hydrogens, with reactants in \( j=0 \), contains the \( E \) and \( A_1 \) representation of the \( D_{3h} \) inversion-permutation group. For the final reactants or products in even \( j' \) also contains \( E \) and \( A_1 \) representations and are therefore difficult to distinguish when using Jacobi coordinates. Finally, the initial case \( j=0 \) and final odd \( j' \) (para-to-ortho transition of dihydrogen molecules/cations) clearly belong to the \( E \) representation of H\(_2\)\(_+\).

Therefore, when using reactant Jacobi coordinates, total integral reaction cross sections can not be obtained, while the para-ortho state-to-state integral cross section can be obtained. However, when referring to H+H\(_2\)\(_+\) (\( v=0, j=0 \)) reaction dynamics we shall include all the cases, physical (\( E \)) and nonphysical (\( A_1 \)), to compare with the D+H\(_2\)\(_+\) (\( v=0, j=1 \)).

III. RESULTS

The reaction probabilities obtained for the three reactions under study for \( J=0 \) are shown in Fig. 3 separated for the three different processes of Eq. 5 and summing over all rotational states of products. The reactions for H+H\(_2\)\(_+\) (left panels), D+H\(_2\)\(_+\) (middle panels) and H+D\(_2\)\(_+\) (right panels) show similar patterns, and each mechanism is discussed separately below.

For the three reactions, the NRCT process (in the top panels of Fig. 3) is open from zero collision energy. As displayed in Fig. 4 the H\(_2\)\(_+\) (\( v=0 \)) classical turning points appear at shorter distances than the crossing point between the H\(_2\)\(_+\) and H\(_2\) potential curves. However, the vibrational ground state of H\(_2\)\(_+\) (\( v=0 \)) and D\(_2\)\(_+\) (\( v=0 \)) have significant amplitude at the region of the crossing, see Fig. 4. This situation allows the electronic charge transfer in the same channel for long \( R \) distances, because the electronic coupling becomes effective (see
FIG. 3. Vibrationally resolved reaction probability for H+H\textsuperscript{2} (v=0, j=0) (left panels), D+H\textsuperscript{2} (v=0, j=0) (middle panels), and H+D\textsuperscript{2} (v=0) (right panels), towards the inelastic charge transfer, NRCT (H+H\textsuperscript{2}, D+H\textsuperscript{2} and H+D\textsuperscript{2}, in the top panels), the exchange reactive channel, ER (H+H\textsuperscript{2}, H+HD\textsuperscript{+} and D+HD\textsuperscript{+}, in the middle panels) and reactive charge transfer, RCT, channels (H\textsuperscript{+}+H\textsubscript{2}, H\textsuperscript{+}+HD and D\textsuperscript{+}+HD, in the bottom panels).

This is particularly evident for H\textsubscript{2}(v'=4) which is nearly resonant with H\textsuperscript{+}+H\textsubscript{2}(v=0) (just 0.064 eV above), presenting a large vibrational overlap, what yields to a strong electronic transition to H\textsubscript{2}(v'=4). The ratio between the final probability in H\textsubscript{2}(v'=4) and all other channels increases with collision energy. This clearly explains the experimental results, who found that charge transfer is the dominant mechanism, rather than hydrogen exchange or complex formation with scrambling. These two mechanisms, associated to ER and RCT, can compete at the lower energies considered here, as discussed below.
For D$_2^+$ (v=0), however, the energy differences with D$_2$(v'=5,6) are larger, of $\approx 0.15$ eV, and the amplitude of the D$_2^+$(v=0) at the electronic crossing is lower (see Fig. 1). All these make less effective the electronic coupling. As a consequence, all the final vibrational channels have lower probability. In spite of the larger energy spacing, the D$_2$(v'=6) level shows to be considerably more populated than any other vibrational level of D$_2$, in clear analogy with the situation of H$_2$.

The exchange reaction mechanism, ER, in the middle panels of Fig. 3 are also non zero, even when it is less probable than the other two charge transfer mechanisms. The adiabatic potential for the first excited electronic state presents a rather high reaction barrier for the exchange. Therefore, ER proceeds in a two step mechanism. First, there is a transition to the ground electronic state, with a deep well, explaining the resonance structure present in the ER probabilities. This is followed by a second transition back to the excited H + H$_2^+/HD^+$/D+DH$^+$ channel, in each case respectively, giving rise to non-zero ER probabilities, lower than the RCT probabilities because there is a lower density of final states for H$_2^+/HD^+$ channels. The probability for the ER channel presents a clear decreases when the mass of reactants increase, from H+H$_2^+$, to D+H$_2^+$ and H+D$_2^+$.

The RCT mechanism (see bottom panels of Fig. 3) consists of two steps, a transition to the ground electronic state and the reactive exchange of a hydrogen atom. Except for H$_2$(v'=4) (or D$_2$(v'=6)), the RCT probabilities are very similar to those of the NRCT channel. This could be explained by the near statistical mechanism of the reaction in the ground adiabatic state$^{24}$ that is, the reaction is mediated by resonances originated by the deep penetration well of the ground electronic state of H$^+$. At collision energies below 1 eV these resonances are long lived and the reaction cross section and the final distribution of products are well described by statistical methods$^{25,26}$. At the higher energies considered here (about 1.8 eV above the ground H$^++$H$_2$ threshold), the resonance persist and a pseudo-statistical behaviour may be expected. This explains the resonance structure of all reaction probabilities in Fig. 3.

Three main differences are found with the previous results recently reported by Ghosh et al.$^{23}$ First, the results of Ref.$^{23}$ do not show the dense manifold of narrow resonances shown here. Also their probabilities do not show a progressive increase with decreasing collision energy, as the present ones do, associated to the long range interactions. Finally, the results of Ghosh et al.$^{23}$ do show a much lower increase of the NRCT for H$_2$(v'=4), and instead their probabilities for H$_2$(v'=3) are of the same order of v'=4. All these differences are attributed to the use of different PESs, and, in particular, to the electronic couplings producing the charge transfer. It is worth noting here, the coupling at relatively long distance plays an important role in the nearly resonant enhancement of the CT for H$_2$(v'=4) obtained here. On the contrary, Ghosh et al.$^{23}$ used a relatively short initial distance of $\approx 5.6$ Å as compared to R$_0=14$ Å used here.

The total reaction probabilities for each of the mechanisms and different values of total angular momentum, J, are shown in Fig. 4 for H+H$_2^+$,D+H$_2^+$ and H+D$_2^+$ reactions. All the probabilities shift towards higher energies with increasing J. However, there are important differences. First, D+H$_2^+$ shows smaller shifts, simply because the effective rotational barrier decreases, because the reduced mass is larger, $\mu \approx 1$, 4/5 and 2/3 amu for D+H$_2^+$, H+D$_2^+$ and H+H$_2^+$, respectively. The NRCT channel also shows a smaller shift with J, what is attributed to the long-range character of the electronic couplings, as described above. Moreover, this also explains why the NRCT probabilities increase near the rotational threshold while for ER and RCT the probabilities clearly decrease with J at the threshold. As the rotational barrier increases, it closes the access to reaction, while the NCR process is still possible due to long range non-adiabatic couplings, which are effective because the quasi-degeneracy of the H$_2^+$ (v=0) and H$_2^+$ (v'=4) levels, or equivalently D$_2^+$ (v=0) and D$_2^+$ (v'=6). This behavior also produces an enhancement of the NRCT mechanism as compared to ER and RCT channels, except for low collisions, where RCT mechanism dominates.

The opacity function, i.e., the reaction probabilities versus J, reported by Ghosh et al.$^{23}$ shows a sudden drop between 0.3 and 0.4 eV at J=12. However, in the present results the rotational threshold at 0.3 eV is approximately at J=40. A continuous and gradual increase of the rotational threshold is found here at all collision energies of Fig. 4. This difference with previous result$^{23}$ is attributed to the long-range behaviour of the electronic couplings and the longer distances considered in the dynamical calculations, as discussed above.

The total integral cross section for each of the processes are shown in Fig. 5 for the H+H$_2^+$ (v=0,j=0) (bottom panel), D+H$_2^+$ (v=0,j=0) (middle panel) and H+D$_2^+$ (v=0,j=0) (top panel) collisions. At 1 eV, $\sigma_{NRCT} > \sigma_{RCT} > \sigma_{ER}$, but the ratio changes with collision energy. The exchange reaction, ER, is always lower, since it involves 2 electronic transitions and the H$_2^+/HD^+$ products have a lower density as compared to H$_2$/HD. The NRCT/ER ratio is nearly constant with collision energy. On the contrary NRCT/RCT varies considerably, being nearly 1 for collision energies near 0.2 eV, and increases to 10/4/9 at 1 eV, for H+H$_2^+$ / D+H$_2^+$ / H+D$_2^+$ respectively. This ratio seems to increase with energy, in agreement with the experiments performed by Karpas et al.$^{65}$, who found that the CT dominates the H+H$_2^+$ reaction.

At low collision energies, before the dominant NRCT resonant H$_2$(v'=4) or D$_2$(v'=6) channel opens, RCT and NRCT cross sections are of the same order, and in most cases the RCT process dominates. In this region the dynamics is dominated by a statistical process: After a first electronic transition, the system gets trapped in the long-lived resonances originated by the deep H$_2^+$ well of the ground electronic state. At these long-lived resonances, energy transfer among all internal degrees of freedom becomes very effective and the products are formed proportionally with the density of states. Thus for H$_2^+$, with three identical H$^+$ + H$_2$ charge transfer products, the NRCT/RCT reaches a factor between 0.5 and 1. For D$^+$ + H$_2$, this factor decreases, since HD$^+$ RCT products have larger density of states than H$_2^+$ + D. Finally, for H+D$_2^+$ the ratio of the density of products states is reversed becoming denser for the inelastic D$_2$ channel than for the reactive HD
one. This explains why here the RCT is nearly identical to NRCT in this case.

The NRCT for the H + D₂⁺ (v=0,j=0) reaction is compared with the experimental work of Andrianarijaona et al.\textsuperscript{66,67} in the top panel of Fig. 5. In these measurements of the H + D₂⁺ reactions, only H⁺ products are detected, so that their cross section only corresponds to the NRCT process. The good agreement obtained with the present results, especially at energies of \( \approx 0.6 \) eV, already demonstrates the adequacy of the simulations done here. It should be noted, however, that the D₂⁺ reactants are produced with some vibrational excitation. This could explain why at lower energies the agreement is
The vibrational resolved cross sections of Fig. 6 are in qualitative agreement with the results in Fig. 7 by Krstić et al., which includes both NRCT and RCT processes calculated in a broader energy range using a close coupling method based on the infinite order sudden approximation (IOSA) with Delves hyperspherical coordinates. In Krstić work, v'=4 cross-section is always the most important, but it becomes of the same order as that for v'=3 at collision energies of 0.2 eV. Below 0.2 eV all σv=0→v' CT cross sections are of the order of 10 Å² and for all v'̸=4 decreases monotonically until 3 eV. At 1 eV the cross section for v'=3 is of the order of 1 Å², similar to the present results of NRCT+RCT. The differences arise about the position of the crossing between v'=4 and the other v', and on the relative magnitude of the cross section associated to different v'. Since the method used here is more accurate, it may be concluded that at energies below 1 eV the present results are more accurate. The calculations of Last et al. were done from 0.06 to 0.21 eV using a quantum method based on negative imaginary
potential combined with a variational quantum method in a $L^2$ basis set. Their NRCT final vibrational distributions pick at $v'=3$, instead of 4. However, they used the helicity decoupling approximation, i.e. they did not consider the coupling between different helicities $\Omega$. In this case, this approximation is not appropriate, because there are strong couplings between the different resonances with different $\Omega$ value originated by the deep well in the ground electronic state. However, the reason why their results are picked at $v'=3$ and not $v'=4$ should be related to the use of different potentials for the $H_2$ and $D_2$ fragments or to the extension of non-adiabatic couplings.

The rotationally resolved NRCT cross sections for $H/D+H^+(v=0,j=0) \rightarrow H^+ + H_2(v'=4,j')$ and $H+D_2^+(v=0,j=0) \rightarrow H^+ + D_2(v'=6,j')$ collisions, in Fig. 7 clearly show that $j'=0$ is the dominant final rotational state, which is the closer to the $H^+_2(v=0,j=0)$ or $D_2^+(v=0,j=0)$ initial state. $j'=2j'=0$ ratio is about a factor of 1/4 for collision energies above 0.3 eV, and this ratio decreases with rotational excitation of CT products. Last et al.\cite{51} also reported the maximum of the state-to-state cross section for final $H_2^+(v'=4,j'=0)$ state, but less than a factor of 2 as compared to $v'=3,j'=4$.

Finally, it should be noted that while the results are accurate for $D+H^+_2$ and $H+D_2^+$, for $H+H^+_2$ we are including also the non-physical $A_1$ irreducible representation. While some work is now in progress to include the full permutation symmetry for $H+H^+_2$, we can already use as exact the para-to-ortho state-to-state cross sections. Moreover, because of the high propensity of the NRCT to final $H_2^+(v'=0,j'=0)$, some conclusions can be extracted. Thus, the present results for $H+H^+_2$ show that the NRCT channel is dominant for energies above 0.2 eV up to 1 eV, in clear agreement with the results of Karpas et al.\cite{46}.

IV. CONCLUSIONS

In this work accurate quantum calculations have been presented for the $H/D+H^+_2$ and $H+D_2^+$ non-adiabatic charge transfer reactions using an accurate 3×3 diabatic potential matrix recently proposed\cite{38} which includes long range interactions. It is found that the dominant channel corresponds to the resonant non-reactive charge transfer from $H^+_2(v=0)$ to $H_2^+(v'=4)$ and $D_2^+(v=0)$ to $D_2(v'=6)$, which is enhanced by their nearly resonant energies and the long-range dependence of the non-adiabatic couplings. This enhancement is based on rather general features of the $H^+_2$ asymptotic features, namely the electronic crossing and the energy difference of the vibrational states of the neutral and cation systems, and are not expected to depend on the accuracy of the PESs used in this work. The only requirement is to include the electronic coupling existing at rather long distances between the reactants, which is described very accurately by the PESs used in this work.

For $D+H^+_2$ and $H+D_2^+$ state-to-state cross sections are presented for the first time. For $H+H^+_2$ some caution must be paid because the permutation symmetry is not fully accounted, while some work is now-a-days in progress to include the permutation among the three fermions. In spite of that, the present results show a good qualitative agreement with the experimental data of Karpas et al.\cite{46} who also reported that the CT channels dominant at $\approx 1.8$ eV. The rather good agreement with the NRCT cross sections measured for $H+D_2^+$ by Andrianarivojona et al.\cite{41,50} already demonstrates the adequacy of the simulations presented here for $E>0.5$ eV. However, a further study on the vibrational effect of the $D_2^+$ reactants should be done to understand the behavior at lower energies. It is also necessary to extend the present calculations to other vibrational states and isotopic variants to provide reaction rate...
constants of interest in astrophysical models of the Early Universe.

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VI. DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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