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Full dimensional potential energy surface for the ground state of H_4^+ system based on triatomic-in-molecules formalism

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In this work, we present a global potential energy surface for the ground electronic state of the H_4^+ based on *ab initio* calculations. The final fit is based on triatomics-in-molecules (TRIM) approximation and it includes extra four-body terms for the better description of some discrepancies found on the TRIM model. The TRIM method itself allows a very accurate description of the asymptotic regions. The global fit uses more than 19 000 multireference configuration interaction *ab initio* points. The global potential energy surface has an overall root mean square error of 0.013 eV for energies up to 2 eV above the global minimum. This work presents an analysis of the stationary points, reactant and product channels, and crossing between the two lowest TRIM adiabatic states. It is as well included a brief description of the two first excited states of the TRIM matrix, concluding that TRIM method is a very good approximation not only for the ground state but also for at least two of the excited states of H_4^+ system. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4827640>]

I. INTRODUCTION

In the interstellar medium (ISM), the dense clouds, circumstellar shell of gas and dust, prestellar cores, etc., are relatively high dense media (10^4 cm^{-3}) with low temperatures ($\approx 10 \text{ K}$). The diffuse conditions during the molecular cloud formation makes very difficult the creation of new molecules. The most abundant molecule in the ISM is the H_2 molecule, it is formed by radiative association of H atoms, and other related reactions as $H^- + H \rightarrow H_2 + e^-$, which are inefficient and not enough to explain the abundance of H_2 . A possible alternative is that H_2 is formed on the surface of dust particles by successive adsorption of H atoms, which seems very efficient as recently reported in experimental and theoretical studies.¹

When a significant amount of H_2 is present, a variety of gas phase reactions with atoms and molecules can occur starting the reaction cycles, giving rise to most of the molecules in the ISM. In the low density regions with low temperatures in the ISM, the three body collisions are negligible and only exothermic reactions with no barrier can occur. Under these conditions, the most efficient reactions involve ions and radicals. Ions are formed by ionization with cosmic rays. For example, H_2 is ionized and reacts with H_2 in the only exothermic and efficient reaction that produces H_3^+ ($H_2^+ + H_2 \rightarrow H_3^+ + H$). This reaction has very high rates even at low temperatures. H_3^+ in turn can collide with another H_2 in a proton transfer reaction which does not destroy H_3^+ . These are the reasons why H_3^+ is the most abundant molecular cation in the ISM and acts as an universal protonator for atoms and molecules. The formation of hydride² cations was explained

by the reaction of H_2 and ionized atoms as O^+ , C^+ , N^+ , etc. Many of these reactions are endothermic³ and just vibrational excitation of H_2 could lead to reaction. As an example, CH^+ has been found in diffuse clouds with low density and FUV radiation, suggesting that maybe the CH^+ is produced by protonation with H_3^+ . Therefore, the study of state-to-state reactivity is necessary to explain how some molecules are formed in very unfavourable conditions.

Because the only direct reaction of formation of H_3^+ comes from the collision between H_2^+ and H_2 , it is important to study the final states of H_3^+ to better understand its spectroscopy and reactivity. From a theoretical point of view, the study of state-to-state collisions of the reaction, $H_2^+ + H_2 \rightarrow H_3^+ + H$, requires the knowledge of the whole potential energy surface (PES). Until now the studies of this reaction had used a local PES^{4–8} or a global Diatomics-in-Molecules (DIM) PES⁹ which fails in the description of the $H_3^+ + H$ product channel. Most of the theoretical studies of the collision between H_2^+ and H_2 are made using quasi-classical trajectories (QCT) on a surface hopping PES.^{10–13} Baer and Ng¹⁴ provided quantum mechanical calculations of reactive and charge transfer cross sections using a reduced 2×2 DIM matrix. The work devoted to the vibrational/rotational distribution of H_3^+ ¹⁵ uses the DIM potential which cannot provide a good description of the H_3^+ . The opposite reaction has not been widely studied, a work based on a local interpolated PES studied the atom exchange of the collision between $H_3^+ + H$.⁷ The collision is studied as well with QCT on a local interpolated PES. Experimentally, the collisions between H_2^+ and H_2 , and isotopologues, have been widely studied. The first studies^{16–21} used different techniques of merged and crossed beams to produce the collision for several ranges of translational

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energies. The new techniques that allowed the state-selection of reactants, produced several experiments where H_2^+ was rotationally or/and vibrationally excited.^{22–28} There are no many studies on the formation of H_4^+ . Due to the exothermicity of the reaction, the creation of H_4^+ is very unlikely. The experimental techniques that have allowed the formation of H_4^+ used beam collisions with H_5^+ molecule²⁹ or formation of even numbered H clusters cations in ultracold helium droplets.³⁰

In this work, we present a new global PES, based on the Triatomics-in-Molecules (TRIM)³¹ method, which describes accurately the H_3^+ fragment and allows the description of eight electronic states. The description of the ground adiabatic state is improved adding two four-body terms, producing a final fit with an accuracy down to few cm^{-1} . The paper is divided as: Sec. II presents the theoretical methodology from *ab initio* calculations to the description of TRIM and global fit. Section III is devoted to the results and discussion and finally Sec. IV presents some conclusions.

II. THEORETICAL METHODOLOGY

A. *Ab initio* calculations and coordinates

The reaction of $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ is exothermic by -1.82 eV. To characterize the full potential energy surface, more than 19 000 *ab initio* points have been calculated. The grids for H_3^+ and H_4^+ are extended from those of H_3^+ ³² and H_4 .³³ A deeper description of the grids is given in the supplementary material.³⁴ The coordinates used throughout in the paper, bond coordinates (in red) and Jacobi coordinates (in blue), are shown in Figure 1. Although the orientation of the molecule is not relevant for the fit of the potential energy, it is given for better comprehension of the Jacobi angles. All points were computed using Molpro package of programs³⁵ with a Dunning augmented correlation-consistent polarised quintuple-zeta basis set (aug-cc-pV5Z).³⁶ The points are calculated using the common complete active space self-consistent field/multireference configuration interaction (MRCI) scheme with no symmetry and where the active space is enlarged gradually until non-apparent change is

FIG. 1. Orientation, bond and Jacobi coordinates for the system of H_4^+ . Bond coordinates in red and Jacobi coordinates in blue.

TABLE I. Atomic, diatomic and asymptotes energies obtained at MRCI level using the aug-cc-pV5Z basis set. Values are compared with the most accurate ones in literature.

System	This work/ E_h	Best/ E_h
H	-0.499995	-0.5 ⁵⁵
H_2	-1.174252	-1.174476 ⁵⁶
H_2^+	-0.602622	-0.602635 ⁵⁷
$\text{H}_3 = \text{H}_2 + \text{H}$	-1.674247	-1.674476
H_3^+	-1.343606	-1.343836 ^{58,59}
$\text{H}_2 + \text{H}_2^+$	-1.776874	-1.777110
$\text{H}_3^+ + \text{H}$	-1.843601	-1.843836
H_4^+	aug-cc-pV5Z	CBS/ E_h
Minimum	-1.852566	-1.852816
TS1	-1.847738	-1.847989
TS2	-1.845781	-1.846038
TS3	-1.838309	-1.838568

obtained in energy. The active space consists of 3 electrons in a total of 14 orbitals, which produce energies very close to full configuration interaction (FCI). Using this basis set and this active space, the MRCI total energy of H_4^+ at its equilibrium geometry is $-1.85256624 E_h$, in perfect agreement with the FCI value of $-1.85256650 E_h$. In Table I are listed some calculated asymptote values and the comparison to the most accurate available values obtained from literature, showing a very good agreement. The absolute errors of the present calculations are 0.236 mE_h (6.42 meV) for the $\text{H}_2 + \text{H}_2^+$ channel and 0.235 mE_h (6.39 meV) for the $\text{H} + \text{H}_3^+$ channel (see Table I). At the bottom of the same table are listed some intermediate stationary points of the H_4^+ using a complete basis set (CBS) extrapolation method based on this of Ref. 37. For the extrapolation method, we have used the aug-cc-pV5Z and aug-cc-pV6Z results.³⁶ The absolute errors between the CBS and the aug-cc-pV5Z results (see Table I) lie in the interval of $0.250\text{--}0.260 \text{ mE}_h$ ($6.80\text{--}7.07 \text{ meV}$). The geometries chosen correspond to the global minimum and 3 transition states which are described in the supplementary material. The absolute errors are nearly constant, what indicates that relative error obtained using the higher (0.260 mE_h) and the lower (0.235 mE_h) absolute errors is of the order of 0.025 mE_h (0.68 meV). Since the global fitting procedure, described next, has a larger error, we may conclude that the aug-cc-pV5Z basis is a good compromise between accuracy and computational cost.

There are several *ab initio* studies of H_4^+ ,^{4,6–8,38–41} however there are only two works devoted to the optimization of stable structures^{40,42} and one about the optimization of stationary points.⁴¹ Jiang and co-workers⁴⁰ found a total of 10 different stable geometrical configurations for H_4^+ but a direct comparison to these calculations is not given here because the basis set and level of calculations (HF/6-311G** and QSCI/6-311G**) used in their study lower accuracy. More recently, an exhaustive study of stationary points was made by Alijah and Varandas⁴¹ using several basis sets at MRCI level. They found a total of four transition states, denoted by TS1, TS2, TS3, and TS4, nomenclature that we adopt here. The structure of these transition states are shown graphically in Fig. 2.

FIG. 2. Configurations of the three transition states optimised. In blue are included the bond distances in angstroms. Equal distances due to symmetry are not included, for TS1 $r_{12} = r_{13}$, $r_{24} = r_{34}$, for TS2 $r_{12} = r_{13} = r_{23}$, $r_{14} = r_{24} = r_{34}$, for TS3 $r_{23} = r_{14}$, $\alpha_{123} = \alpha_{214}$, and for TS4 $r_{12} = r_{34}$, $r_{13} = r_{14} = r_{23} = r_{24}$.

A deeper description of these transition states and comparison with our results is given in the supplementary material.³⁴

B. DIM treatment

The only analytical form available for the description of the global potential energy surface of the ground electronic state of H_4^+ system is the DIM representation developed by Stine and Muckerman.⁹ Here, we rederived the DIM equations but using an orthonormal basis set, based on a cyclic description of the elements.

For three electrons system, there are two combinations with total spin $S = 1/2$ and $M_s = +1/2$ (degenerate with the $M_s = -1/2$), whose eigenfunctions are $S_1 = (\alpha_1\beta_2\alpha_3 - \beta_1\alpha_2\alpha_3)/\sqrt{2}$ and $S_2 = (2\alpha_1\alpha_2\beta_3 - \alpha_1\beta_2\alpha_3 - \beta_1\alpha_2\alpha_3)/\sqrt{6}$ which can be written in general form as

$$S_I = \sum_{\sigma} C_{\sigma}^I \sigma_1 \sigma_2 \sigma_3. \quad (1)$$

The orbital part is described by a minimum basis set, with one 1s function in each H atom, giving rise to four functions ϕ_i , where i denotes one electron hole on nuclei i , and one electron in each 1s function of the rest of nuclei, expressed as

$$\phi_i = s_j(1)s_k(2)s_l(3) \text{ with } \begin{cases} i, j, k, l = 1, \dots, 4 \text{ cyclic} \\ j = i + 1, k = i + 2, l = i + 3. \end{cases} \quad (2)$$

The total basis set obtained from the direct product of the spin and orbital functions is composed of eight functions of the form

$$\Psi_{iI} = \mathcal{A} \phi_i S_I \quad (3)$$

corresponding to linear combinations of Slater determinants, where $\mathcal{A}$ is the antisymmetrization operator.

The electronic Hamiltonian is partitioned in atomic and diatomic fragments as

$$\hat{H}_e \equiv \hat{H}_e^i = \hat{H}_{ij}^+(1) + \hat{H}_{ik}^+(2) + \hat{H}_{il}^+(3) + \hat{H}_{jk}(1, 2) + \hat{H}_{jl}(1, 3) + \hat{H}_{kl}(2, 3) + \mathcal{O}, \quad (4)$$

corresponding to a hole in nuclei i , and where the $\hat{H}_{ik}^+$ are the mono-electronic Hamiltonians of the H_2^+ fragments (being i, k the nuclei involved), and $\hat{H}_{jk}$ are the bielectronic Hamiltonians describing H_2 fragments jk , and $\mathcal{O}$ denotes the atomic fragments.

The Hamiltonian matrix elements $\langle \Psi_{i'I'} | H_e | \Psi_{iI} \rangle$ are calculated following the procedure already explained for H_5^+ ,³¹ considering the reduction of electrons and nuclei. The resulting Hamiltonian matrix is factorised as

$$\mathbf{H} = \begin{pmatrix} \mathcal{H}^{11} & \mathcal{H}^{12} \\ \mathcal{H}^{21} & \mathcal{H}^{22} \end{pmatrix}, \quad (5)$$

where now the individual elements of this matrix are 4×4 matrices. $\mathcal{H}^{11}$ and $\mathcal{H}^{22}$ correspond to the first and second spin components, respectively, and $\mathcal{H}^{12}$ to the matrices between different spin functions. The three matrices have the form

$$\mathcal{H}^{11} = \begin{pmatrix} \mathcal{H}_{11}^{11} & -\Delta^+(r_{12})/2 & -\Delta^+(r_{13})/2 & -\Delta^+(r_{14})/2 \\ -- & \mathcal{H}_{22}^{11} & -\Delta^+(r_{23})/2 & -\Delta^+(r_{24})/2 \\ -- & -- & \mathcal{H}_{33}^{11} & -\Delta^+(r_{34})/2 \\ -- & -- & -- & \mathcal{H}_{44}^{11} \end{pmatrix} \quad (6)$$

with $\mathcal{H}_{ii}^{11} = \Sigma^+(r_{ij}) + \Sigma^+(r_{ik}) + \Sigma^+(r_{il}) + V_{i\Sigma}(r_{jk}) + \Sigma_3(r_{jl}) + \Sigma_3(r_{kl})$,

$$\mathcal{H}^{22} = \begin{pmatrix} \mathcal{H}_{11}^{22} & -\Delta^+(r_{12})/2 & \Delta^+(r_{13})/2 & -\Delta^+(r_{14})/2 \\ -- & \mathcal{H}_{22}^{22} & -\Delta^+(r_{23})/2 & \Delta^+(r_{24})/2 \\ -- & -- & \mathcal{H}_{33}^{22} & -\Delta^+(r_{34})/2 \\ -- & -- & -- & \mathcal{H}_{44}^{22} \end{pmatrix} \quad (7)$$

with $\mathcal{H}_{ii}^{22} = \Sigma^+(r_{ij}) + \Sigma^+(r_{ik}) + \Sigma^+(r_{il}) + V_{i\Sigma}(r_{jk}) + \Sigma_1(r_{jl}) + \Sigma_1(r_{kl})$ and

$$\mathcal{H}^{12} = \begin{pmatrix} \mathcal{H}_{11}^{12} & -\Delta^+(r_{12})\sqrt{3}/2 & \Delta^+(r_{13})\sqrt{3}/2 & \Delta^+(r_{14})\sqrt{3}/2 \\ -- & \mathcal{H}_{22}^{12} & -\Delta^+(r_{23})\sqrt{3}/2 & \Delta^+(r_{24})\sqrt{3}/2 \\ -- & -- & \mathcal{H}_{33}^{12} & -\Delta^+(r_{34})\sqrt{3}/2 \\ -- & -- & -- & \mathcal{H}_{44}^{12} \end{pmatrix} \quad (8)$$

with $\mathcal{H}_{ii}^{12} = [\Delta^+(r_{jl}) - \Delta^+(r_{kl})]\sqrt{3}/2$. All the diatomic matrix elements of the type $\Sigma^+(r_{ij})$, $\Delta^+(r_{ij})$, $V_{i\Sigma}$, ..., depending on the r_{ij} internuclear distances are simple functions of the H_2 and H_2^+ eigenvalues, and its explicit forms are given in the Appendix of Ref. 31.

C. TRIM treatment: H_3^+ matrix elements and long range interactions

The DIM treatment cannot accurately describe the H_3^+ fragment. Here, we shall use a generalization of this approach,

the TRIM, which includes three-atoms interactions improving the accuracy in the $\text{H}_3^+ + \text{H}$ channel. This TRIM approach has been successfully used in the description of H_5^+ .³¹ Similar to what it was done for H_5^+ ,³¹ the Hamiltonian is partitioned as

$$\hat{H}_e^i = \sum_{n>i, o>n} \hat{H}_{ino}^+(n-i, o-i) - \sum_{p>i} \hat{H}_{ip}^+(p-i), \quad (9)$$

where H_{ip}^+ are the mono-electronic Hamiltonians of H_2^+ fragments, already given in Eq. (4) in the DIM approximation, $H_{ino}^+(n-i, o-i)$ are the bi-electronic Hamiltonians (for $n-i, o-i$ electrons) describing the H_3^+ system for the *ino* nuclei.

Using the same electronic and spin basis set as given in Eqs. (1) and (2), the $\langle \Psi_{i'l'} | \hat{H}_e | \Psi_{il} \rangle$ matrix elements are calculated following the procedure described in Ref. 31. The resulting Hamiltonian matrix is a 8×8 matrix and is factorised as in Eq. (5), whose individual elements are

$$\mathcal{H}_{ii}^{11} = H_{11}^0(r_{ij}, r_{jk}, r_{ki}) + \Sigma_{11}^1(r_{ij}, r_{jl}, r_{li}) + \Sigma_{11}^1(r_{ik}, r_{kl}, r_{li}) - \Sigma^+(r_{ij}) - \Sigma^+(r_{ik}) - \Sigma^+(r_{il}),$$

$$\mathcal{H}_{ji}^{11} = -\frac{1}{2}H_{21}^0(r_{ij}, r_{jk}, r_{ki}) + \Sigma_{21}^1(r_{ij}, r_{jl}, r_{li}) + \frac{1}{2}\Delta^+(r_{ij}),$$

$$\mathcal{H}_{ki}^{11} = -\frac{1}{2}[H_{21}^0(r_{ik}, r_{kl}, r_{li}) + H_{31}^0(r_{ij}, r_{jk}, r_{ki}) - \Delta^+(r_{ik})],$$

$$\mathcal{H}_{li}^{11} = -\frac{1}{2}H_{31}^0(r_{ij}, r_{jl}, r_{li}) + \Sigma_{31}^1(r_{ik}, r_{kl}, r_{li}) + \frac{1}{2}\Delta^+(r_{il}),$$

$$\mathcal{H}_{ii}^{22} = H_{11}^1(r_{ij}, r_{jk}, r_{ki}) + \Sigma_{11}^0(r_{ij}, r_{jl}, r_{li}) + \Sigma_{11}^0(r_{ik}, r_{kl}, r_{li}) - \Sigma^+(r_{ij}) - \Sigma^+(r_{ik}) - \Sigma^+(r_{il}),$$

$$\mathcal{H}_{ji}^{22} = \frac{1}{2}H_{21}^1(r_{ij}, r_{jk}, r_{ki}) - \Sigma_{21}^0(r_{ij}, r_{jl}, r_{li}) + \frac{1}{2}\Delta^+(r_{ij}),$$

$$\mathcal{H}_{ki}^{22} = -\frac{1}{2}[H_{21}^1(r_{ik}, r_{kl}, r_{li}) + H_{31}^1(r_{ij}, r_{jk}, r_{ki}) + \Delta^+(r_{ik})],$$

$$\mathcal{H}_{li}^{22} = \frac{1}{2}H_{31}^1(r_{ij}, r_{jl}, r_{li}) - \Sigma_{31}^0(r_{ik}, r_{kl}, r_{li}) + \frac{1}{2}\Delta^+(r_{il}),$$

$$\mathcal{H}_{ii}^{12} = \frac{\sqrt{3}}{2}[\Delta_{11}(r_{ij}, r_{jl}, r_{li}) - \Delta_{11}(r_{ik}, r_{kl}, r_{li})],$$

$$\mathcal{H}_{ji}^{12} = \frac{\sqrt{3}}{2}[-H_{21}^1(r_{ij}, r_{jk}, r_{ki}) + \Delta_{21}(r_{ij}, r_{jl}, r_{li}) - \Delta^+(r_{ij})],$$

$$\mathcal{H}_{ki}^{12} = \frac{\sqrt{3}}{2}[H_{21}^0(r_{ik}, r_{kl}, r_{li}) - H_{31}^1(r_{ij}, r_{jk}, r_{ki}) - \Delta^+(r_{ik})],$$

$$\mathcal{H}_{li}^{12} = \frac{\sqrt{3}}{2}[-H_{31}^0(r_{ij}, r_{jl}, r_{li}) - \Delta_{31}(r_{ik}, r_{kl}, r_{li}) + \Delta^+(r_{il})].$$

In these equations, all the $\Sigma^+(r_{ij})$, $\Delta^+(r_{ij})$, $V_{i\Sigma}, \dots$, diatomic matrix elements, depending on a single r_{ij} distance, correspond to simple linear combinations of the eigenvalues of H_2^+ fragments, and are given in the Appendix of Ref. 31.

The $H_{11}^0(r_{ij}, r_{jk}, r_{ki})$, $\Sigma_{11}^1(r_{ij}, r_{jk}, r_{ki})$, $\dots$, triatomic matrix elements depend on three internuclear distances and are simple functions of the 3×3 diabatic matrices, representing H_3^+ fragments in the singlet or triplet electronic states. The explicit expressions are given in the Appendix of Ref. 31. The 3×3 diabatic matrices of H_3^+ are approximated following the same procedure as published for H_5^+ .³¹ The first three adia-

batic eigenvalues, E_j^S (where $S = 0, 1$ denotes the spin, and j the eigenvalue) are described as^{43,44}

$$E_j^S(r_{ij}, r_{jk}, r_{ki}) = E_j^{S,DIM}(r_{ij}, r_{jk}, r_{ki}) + W_S(r_{ij}, r_{jk}, r_{ki}), \quad (10)$$

where $E_j^{S,DIM}$ are the eigenvalues of the DIM matrix built for H_3^+ for $S = 0$ or 1 . Here, we use two approximations. First, we consider that the three-body correction W_S is the same for the three states of the same spin S . Second, we use the DIM eigenvectors to transform from the H_3^+ adiabatic representation to the diabatic one used to build the TRIM matrix elements.³¹ This procedure allows to describe very accurately the ground state of the H_3^+ fragments in either the singlet or triplet state. However, it introduces some errors for the description of excited states.

One advantage of this approach is that it allows to improve the description of long range interactions in systems where the charge is delocalized between different fragments, requiring a multi-state description.⁴⁵⁻⁴⁷ The H_4^+ system is described as a linear combination of several H_3^+ fragments, using a diabatic representation in which the charge is localized in a particular nuclei i . Thus, the description of the long range interactions in the $\text{H}_2 + \text{H}_2^+$ and $\text{H} + \text{H}_3^+$ fragmentation channels is done through the 3×3 H_3^+ diabatic matrices. Furthermore, these matrices include the ion-induced-dipole and ion-quadrupole $\text{H}^+ + \text{H}_2$ and $\text{H} + \text{H}_2^+$ long range interactions in the diagonal matrix elements of the 3×3 diabatic matrix, as described in Refs. 31 and 45.

D. Global PES fitting

In order to include four-body interactions missing in the TRIM treatment, the potential energy surface for the ground electronic state of H_4^+ is described as

$$V_{H_4^+} = V_{TRIM} + \sum_N^{NMAX=2} V_{ABCD}^{(4)N}(R_{AB}, R_{AC}, \dots), \quad (11)$$

where V_{TRIM} is the ground eigenvalue of the TRIM matrix, and V_{ABCD} are four-body terms. In this case, $NMAX = 2$ implies that we use four body terms for the fit. This procedure is an extension of the methods previously used to describe H_3^+ ^{43,44} and H_5^+ .³¹ The many-body terms are described following the method of Refs. 48–51, and applied to a wide variety of triatomic systems.⁵²⁻⁵⁴ In this case, to account for the permutation invariance, the four-body terms are expressed as linear combinations of symmetry adapted functions as^{42,50,51}

$$V_{ABCD}^{(4)N}(R_{AB}, R_{AC}, R_{AD}, \dots) = \sum_{ijk\dots n}^M f_{ij\dots n}^M \mathcal{W}_{ABCD}^4 \rho_{AB}^i \rho_{AC}^j \rho_{AD}^k \dots \rho_{CD}^n, \quad (12)$$

where $\mathcal{W}^4$ are Young operators for the totally symmetric irreducible representation of the S_4 permutation group, needed to warranty that the PES is symmetric under permutation of identical nuclei. The $\rho_{\beta\eta} = R_{\beta\eta} e^{-\gamma_{\beta\eta} R_{\beta\eta}}$ are Rydberg-type functions defined in terms of the internuclear distance $R_{\beta\eta}$.

TABLE II. Number of points used on each individual fit, degree, and rms obtained for the two-, three-, and four body terms fitting. The rms values are given in eV. The values included in parenthesis specify the total number of three- or four-body terms for correspondent fits.

System	H ₂	(H ₂) ⁺	H ₂ ⁺	(H ₂) ⁺ *	H ₃ ⁺	(H ₃) ⁺ *	H ₄ ⁺
State	¹ Σ _g ⁺	³ Σ _u ⁺	² Σ _g ⁺	² Σ _u ⁺	¹ A'	³ A'	² A'
N _{pts}	110	110	112	112	7610	5995	6074
Degree	10	10	10	10	6	12 (3)	7 (2)
rms	6.0 × 10 ⁻⁵	0.00161	6.7 × 10 ⁻⁵	0.0071	0.0016	0.0052	0.013

III. RESULTS AND DISCUSSION

A. Analysis of fitting error

The final analytical representation of the ground electronic state PES of H₄⁺ needs several many-body terms. DIM method requires the fit of the H₂ and H₂⁺ two-body terms. TRIM method uses the H₃⁺ three-body terms for singlet and triplet states. In addition, to increase the accuracy of the global fit we have added four-body terms. The details of the different fits, as number of points used, degree of the polynomial, and root-mean-square (rms) error, are listed in Table II. As expected, the rms error increases with the complexity of the system.

In order to analyze the progressive improvement of the DIM, TRIM, and global fit representations of the ground PES, the rms errors of the three methods are listed in Table III, divided in energy intervals. The energy origin hereafter is placed at the minimum of the H₂ and H₂⁺ fragments, when they are infinitely separated. The H₃⁺ + H asymptote is at -1.82 eV, and the global minimum (see Fig. 2) at -2.06 eV. The DIM method on its own, although giving a rather good qualitative representation of the surface, gives the highest error for all subsets. DIM method underestimates the global minimum and cannot reproduce well the exothermicity of the reaction because the approximation cannot describe the three-body interactions (see Table III). This last disagreement is corrected within the TRIM approximation since the Hamiltonian includes the three-body interactions, nonetheless the minimum interaction region is overestimated using TRIM method. Even with this anomaly found near the global minimum, the TRIM approximation produces a better description of the whole surface and this is shown in the decreasing of the rms for all subsets of energy. The global fit, which includes two four-body terms to the TRIM approximation, improves further the errors for all subsets. In the energy interval going from the global minimum (-2.06 eV) up to 2 eV (above H₂ + H₂⁺ channel), the error is 0.013 eV. It should be noted that

this energy interval includes several conical intersections (CI) as described below, at which cusp the fit presents a relatively high error.

In Fig. 3, we show the comparison of DIM, TRIM, and global fit PESs with respect to the MRCI calculated energies. In the top panel are plotted the residuals (algebraic deviations) as a function of the energy, up to 2 eV above the zero of energy. In the bottom panels are represented the energies of the fit with respect to the MRCI energies. There is a progressive decreasing of the error from DIM to global fit of more than one order of magnitude in the region of interest.

B. Asymptotic H₂ + H₂⁺ region

The asymptotic behavior of the approaching of H₂ and H₂⁺ can be analyzed producing cuts in the surface keeping the internuclear distances fixed. In Fig. 4 are plotted the cuts of the surface as a function of *R* for different Jacobi angles (see Figure 1) when H₂ and H₂⁺ are fixed in their equilibrium distances (*r*₁ = 0.740 Å, *r*₂ = 1.055 Å). The top panels correspond to a parallel approach, the two middle panels are the two possible t-shaped approaches, and the bottom panels correspond to the linear approach. The long range part (in the right panels) is very well described by the TRIM approach, and hence by the global FIT, down to 6 Å. For shorter distances, TRIM method starts to separate from the *ab initio* calculations, and this deviation is corrected by the global fit. The DIM method is also rather good but only for distances longer than *R* = 8 Å. Below this value it shows a larger difference with respect to the *ab initio* points than the TRIM. It should be noted that the DIM clearly overestimates the barriers present at the two bottom panels, what makes very difficult to obtain a global fit using the DIM matrix as a zero order description in Eq. (11).

In the left panels, for short and intermediate values of *R*, three body terms start to play a role, and the DIM clearly deviates from *ab initio*, being unable to reproduce the deep attractive interaction describing H₃⁺ evident in the middle-top panels for θ₁ = 90 and θ₂ = 0. The TRIM, on the contrary, describes pretty well this attractive interaction for all the configurations shown. This makes possible to improve the accuracy of the global fit, which shows a very good agreement with the calculated *ab initio* points.

It should be noted that the situation gets much more complicated when the two diatomic distances are equal. In such situation, the charge can be in either of the two diatomic fragments. Thus, at infinite *R* values there is a crossing, because there is no interaction between fragments. As *R* gets shorter, the interaction between the two diatomic fragments

TABLE III. Accuracy of DIM, TRIM, and global fit for several subsets of *ab initio* energy intervals. Energies and rms are given in eV and the zero of energy corresponds to the asymptote of H₂ + H₂⁺.

Subset	Energies	N _{pts}	rms _{DIM}	rms _{TRIM}	rms _{Global}
Energies below H ₃ ⁺ ... H	-2.06 ≤ E ≤ -1.82	1577	0.27	0.016	0.00098
Energies below H ₂ ... H ₂ ⁺	-1.82 ≤ E ≤ 0.0	2660	0.51	0.099	0.0084
Energies up to 2 eV	0.0 ≤ E ≤ 2.0	1837	0.63	0.15	0.029
All energies	-2.06 ≤ E ≤ 2.0	6074	0.48	0.093	0.013

FIG. 3. Comparison of the DIM (left panel), TRIM (centre panel), and fitted (right panel) global PESs of H_3^+ with the MRCI energies. On the three top panels are plotted the residuals (algebraic deviations) vs the energy. On the three bottom panels are the analytical energies with respect to the MRCI energies.

becomes non-negligible and the crossing becomes avoided. This is clearly seen in the right panels of Fig. 5, at $R = 4 \text{ \AA}$ and $\theta_1 = 90, \theta_2 = 0 = \phi_1 = \phi_2$. The lowest energy crossing is found when both internuclear distances are $0.87 \text{ \AA}$, with an energy of 0.47 eV above the zero or energy, considered in the reactant channel. For $R = 3 \text{ \AA}$ (middle panel of Fig. 5), the interaction between diatomic fragments becomes stronger and the two states become more separated in energy, and for $R = 2 \text{ \AA}$ the crossing is between the second and third root, indicating that the charge transfer involves other atoms. In Fig. 5, it is clear that both DIM and TRIM methods describe very well the crossing for $R > 3 \text{ \AA}$. At shorter distances, $R = 2 \text{ \AA}$, the TRIM method describes better than DIM the ground and the excited electronic potentials. However, the disagreement between TRIM and *ab initio* results increases at the cusps of the crossings. These cusps are due to many CI seams present in this system, clearly identified at the most symmetric configurations.

In a CI, the non-adiabatic couplings diverge, and the description is easier using the diabatic representation. Since the lower crossing occurs just 0.47 eV above the zero or energy, it is necessary to study non-adiabatic dynamics near and above this energy. Until now, most of the dynamical calculations have been performed using the surface hopping approximation^{10–13,15} on whole 8×8 DIM diabatic matrix. Furthermore, Baer and Ng¹⁴ developed a two coupled diabatic states corresponding to the 2 lowest eigenvalues of the DIM matrix.

We can conclude that this TRIM method provides, not only, a better diabatic description of triatomic products channel, but as well of entrance channel (see Fig. 5) in the ground and first excited states.

C. From minimum to asymptotic $\text{H}_3^+ + \text{H}$ region

As it has already been mentioned, the $\text{H}_3^+ + \text{H}$ channel is poorly described by the DIM method. DIM method over-

FIG. 4. Cut of the PES as a function of R , keeping H_2 and H_3^+ in their equilibrium distances $r_1 = 0.740 \text{ \AA}$, $r_2 = 1.055 \text{ \AA}$, for different orientations θ_1 and θ_2 for $\phi_1 = \phi_2 = 0$. Left panels show short distances while right panels show the long distance region. *Ab initio* points (empty circles) are compared with the values of DIM, TRIM, and global fit.

estimates the binding energy of H_3^+ by $\approx 0.35 \text{ eV}$. On the contrary, the DIM method underestimates the binding energy of the global minimum, and presents a very shallow well at much longer distances (see left panels of Fig. 6). The TRIM method describes correctly the $\text{H}_3^+ + \text{H}$ asymptotic energy, and the long range interaction between H_3^+ fragments and H atom, as can be seen in the right panels of Fig. 6. However, TRIM method overestimates the binding energy of the global well $\approx 0.2 \text{ eV}$, although the well appears at approximately the same geometries. This fact allows to get an accurate global fit, which describes very well this well, corresponding to a H atom interacting with a distorted H_3^+ . The minimum of the well corresponds to the geometry depicted in Fig. 2, with a binding energy of $\approx 0.245 \text{ eV}$ with respect to the $\text{H}_3^+ + \text{H}$ asymptote, while the *ab initio* value is 0.244 eV , either using the CBS or the aug-cc-pV5Z basis sets as listed in Table I. This dissociation energy is very similar to the one published by Moyano and co-workers⁷ and Alijah and Varandas,⁴¹ both values of 0.24 eV obtained with the same basis set and similar level of calculation.

In Fig. 7 is plotted the motion of H atom around the triangular H_3^+ molecule. The geometry of H_3^+ is fixed on the values of the global minimum (see Table I in the supplementary material³⁴) for both panels. The left panel, representing the in-plane rotation of H atom around the H_3^+ , presents two minima. In this figure, the geometry of the H_3^+ is fixed, so this is the reason why the second minimum at $(-2, 1.8) \text{ \AA}$ is

FIG. 5. Potential energy of the ground and first excited states as a function of r_1 distance for several values of r_2 and R (in Angstroms), for $\theta_1 = \pi/2$, $\theta_2 = 0$, and $\phi_1 = \phi_2 = 0$. Each row represents a constant value of r_2 and each column a constant value of the inter-molecule R distance. The DIM, TRIM, and global fit are compared with the *ab initio* points.

shallower. In the right panel is plotted the out-of-plane rotation that shows on the right of the plot the global minimum, and on the left the minimum corresponding to a similar geometry to this of TS1 transition state.

D. Minimum energy path (MEP) for the ground and two excited states

The MEPs for the ground and two first excited states are shown in Fig. 8. That of the ground state has been calculated using the global fit, while those of the first and second excited states were optimized independently using the second and third eigenvalues of the TRIM matrix, respectively. The DIM (red), TRIM (green), and *ab initio* (points) eigenvalues are compared for the three electronic states, while the global fit is only shown for the ground electronic state. In addition, in Table IV are compared the *ab initio* values with the DIM, TRIM, and global fit along the minimum energy path.

The ground state corresponds to the $\text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+(\text{A}')$ + H reaction, exoergic by 1.82 eV, whose features have already been described above. The global fit matches the *ab initio* points, and the TRIM describes very well the calculated points except in the absolute well minimum where it overestimates the binding energy. The DIM results differ signifi-

cantly in describing the absolute minimum and the products channel.

The first excited state is highly endothermic, with a difference of energy between reactants and products of 2.32 eV. It presents a barrier in the entrance channel of 1.87 eV, above the reactants, and a global minimum of 2.27 eV below the products channel. The geometry of the minimum is an equilateral triangle, with stretched sides, in which the fourth atom is placed in the middle of the triangle ($r_{12} = 1.780$, $r_{13} = 1.027$, $r_{14} = 1.780$, $r_{23} = 1.027$, $r_{24} = 1.780$, $r_{34} = 1.027$ Å). The products correspond to neutral H_3 and H^+ fragments, where H_3 is not bound, i.e., it corresponds to $\text{H}_2(^1\Sigma_g^+) + \text{H} + \text{H}^+$. Because the entrance and exit channels end in states of the atomic and diatomic systems, both DIM and TRIM methods describe well these asymptotes. We have to point out that the same asymptote of $\text{H}_2 + \text{H} + \text{H}^+$ should appear as reactants in the MEP of some excited states. However, because the MEPs in Fig. 8 are calculated directly from the adiabatic states of the TRIM matrix, the optimization can find the lowest energy in different configurations, where many crossings may have happened.

In order to give an idea of the crossings occurring within the TRIM states, several monodimensional cuts of the PES are presented in Fig. 9. The distances used in the plot are indicated in the figure for a T-shape configuration

FIG. 6. Potential energy as a function of R_r , the distance between the H_3^+ center of mass and the fourth H atom, for long distances (right panels) and short distances (left panels). Three different angular configurations are considered, as indicated in the inset, corresponding to the absolute minimum (top panels), TS1 (middle panels), and TS2 (bottom panels).

($\theta_1 = 90^\circ$, $\theta_2 = \phi_1 = \phi_2 = 0^\circ$). In this figure, we can follow easier the adiabatic states, and see the correlation between reactants and products through the different crossings.

The second excited state is exothermic by just 0.36 eV and presents a global minimum in a linear configuration ($r_{12} = 0.967$, $r_{13} = 1.765$, $r_{14} = 3.864$, $r_{23} = 1.282$, $r_{24} = 2.897$, $r_{34} = 1.615$ Å). The depth of the minimum is 0.64 eV below the product channel (1.00 eV below the entrance channel).

FIG. 7. Contour plots of the PES as a function of $X = R_r \sin \theta$ and $Z = R_r \cos \theta$, with θ being the angle describing the rotation of H atom in plane (left panel) or outplane (right panel). The blue lines drawn in the X-axis represent the molecule and the plane in which the H atom is moving. The contours run from -2.04 to -1.5 in intervals of 0.02 eV.

The MEP of the second excited state shows the reaction between a $\text{H}_2(^1\Sigma_g^+)$ ($r = 0.925$ Å) and a dissociative $\text{H}_2(^2\Sigma_u^+)$, producing a linear H_4^+ molecule which dissociates to $\text{H}_3^+(^3A')$ + H. The excited $\text{H}_3^+(^3A')$ molecule has a linear geometry,⁴⁴ structure that explains the formation of a stable linear H_4^+ . In Fig. 8 is plotted the TRIM optimized MEP for this state, compared to the third root of the DIM matrix and the calculated *ab initio* points. In the entrance channel, where reactants only consist of diatomic and atomic systems, both DIM and TRIM methods agree perfectly with the calculated points. However, in the product channel the reaction produces excited $\text{H}_3^+(^3A')$, and for the same reason as in the ground state the DIM method cannot reproduce well the triatomic fragments. On the contrary, the TRIM results are in a reasonably good agreement with the *ab initio* data. It may be concluded that TRIM method not only supposes a good first approximation to the ground state, but as well it can be used as a good first approximation to at least the two first excited states of the H_4^+ system.

IV. CONCLUSIONS

In this paper, we present the first global fit of the PES of the ground state of the $\text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H}$ reaction, based on *ab initio* points at MRCI level. The surface describes very accurately the whole surface with a total error of 0.013 eV. The $\text{H}_3^+ + \text{H}$ asymptote was not well reproduced by the DIM method, the only global PES for this reaction until now. In this work, the description of this asymptote has been significantly improved by the use of the TRIM method, a generalization of the DIM method first implemented for the H_5^+ .³¹ TRIM method produces the PES from a Hamiltonian that is a linear combination of all possible triatomic fragments present in the system.

TRIM model describes qualitatively well the whole surface, just overestimating the global minimum. This disagreement is removed adding four-body terms producing a global fit which provides a very accurate PES. A brief description of the at least two excited states, obtained as the second and

FIG. 8. Minimum energy path calculated individually for the ground and the two first excited states. The ground state is obtained from the global fit and the excited states from the first and second roots of the TRIM matrix. $r_e^{H_2} = 0.74$, $r_e^{H_2^+} = 1.0$, $r_c = 0.87$, and $r_{el} = 0.92$ Å.

TABLE IV. Calculated and fitted energies along the minimum energy path. Distances are in Å and energies in eV.

	$H_2 + H_2^+$	TS4	TS3	H_4^+	TS1	TS2	$H_3^+ + H$
$E_{ab\ initio}$	0.0	-1.315	-1.672	-2.060	-1.927	-1.875	-1.815
E_{DIM}	0.0	-0.507	-0.924	-1.738	-2.072	-2.116	-2.094
E_{TRIM}	0.0	-1.022	-1.583	-2.219	-2.014	-1.918	-1.815
E_{fit}	0.0	-1.327	-1.671	-2.060	-1.925	-1.877	-1.815

FIG. 9. TRIM electronic states from reactants to products for a fixed H_2 distance ($r_1 = r_{H_2} = 0.74$ Å). The left panel shows the variation of r_2 with a constant value of $P_3 = 25$ Å. The central panel shows the variation of P_3 for a constant value of $r_2 = 25$ Å and the third panel shows the variation of r_2 for a constant value of $P_3 = 0.74$ Å.

third adiabatic states of the TRIM matrix, shows that TRIM method can be a good first approach in the description of excited states of H_4^+ .

We thus conclude that TRIM method provides a 8×8 diabatic representation for this system, improving significantly the DIM case, and allowing to describe the non-adiabatic processes, expected to be important above 0.46 eV.

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