Toward a realistic density functional theory potential energy surface for the H_5^+ cluster

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The potential energy surface of H_5^+ is characterized using density functional theory. The hypersurface is evaluated at selected configurations employing different functionals, and compared with results obtained from *ab initio* CCSD(T) calculations. The lowest ten stationary points (minima and saddle-points) on the surface are located, and the features of the short-, intermediate-, and long-range intermolecular interactions are also investigated. A detailed analysis of the surface's topology, and comparisons with extensive CCSD(T) results, as well as a recent *ab initio* analytical surface, shows that density functional theory calculations using the B3(H) functional represent very well all aspects studied on the H_5^+ potential. These include the tiny energy difference between the minimum at 1- C_{2v} configuration and the 2- D_{2d} one corresponding to the transition state for the proton transfer between the two equivalent C_{2v} minima, and also the correct asymptotic behavior of the long-range interactions. The calculated binding energy and dissociation enthalpies compare very well with previous benchmark coupled-cluster *ab initio* data, and with experimental data available. Based on these results the use of such approach to perform first-principles molecular dynamics simulations could provide reliable information regarding the dynamics of protonated hydrogen clusters. © 2010 American Institute of Physics. [doi:10.1063/1.3466763]

I. INTRODUCTION

The protonated hydrogen clusters, $H_3^+(H_2)_n$, along with their fundamental interest as benchmark systems are also of considerable present day relevance for modeling planetary atmospheres and interstellar clouds,^{1–3} for nuclear fusion reactions^{4,5} and energetic Coulomb explosions,⁶ as well as for a possible medium for energy storage.^{7,8} The first and most stable member of the cluster series, the H_5^+ , has been the subject of a numerous theoretical^{9–27} and experimental^{28–34,36} studies. All theoretical high-level *ab initio* studies predict the asymmetric C_{2v} structure as the global minimum on the H_5^+ surface, while recent Monte Carlo calculations have shown that the zero-point averaged structure corresponds to the symmetric D_{2d} geometry,²⁷ with the proton in the middle of the two H_2 diatoms. However, apart from theoretical predictions on its structure and energetics, the present experimentally confirmed knowledge of the ion is still rather limited. The available molecular spectra,^{32,34} which consist of broad rotationally unresolved bands, only provide few vibrational frequencies of H_2 and H_3^+ stretching modes, while various experimental^{28–31,37–39} data are available for dissociation enthalpies and entropies for the $H_3^+ + H_2 \rightarrow H_5^+$ clustering reaction. More recently, new experimental infrared photodissociation spectra have also reported.³⁵ From these spectra vibrational frequencies associated with the shared-proton stretch mode have been assigned, and upper limits for the dissociation energies (D_0) for

the H_5^+ and D_5^+ ions have been also established.³⁵ In addition, several experimental studies of $H_3^+ + HD$ reaction and its isotopic analogs have been performed.^{40–42} Rate coefficients even at typical interstellar cloud temperatures have been measured by Gerlich *et al.*,² and recently new experimental data in the temperature range of 5–50 K have been reported by Hugo *et al.*⁴³ Comparisons of predicted and observed values support that such type of gas-phase reactions is less efficient than it had been expected, indicating that different temperature-dependent mechanisms should be concerned.^{21,25,43,44} Thus, in view of experimental difficulties to establish the spectroscopic characterization of H_5^+ , and its role in the gas-phase ion-molecule reaction mechanism, more extended and laborious theoretical predictions are required in order to assist further experimental investigations.

A key point for carrying out rigorous dynamics calculations to explore gas-phase solvation, cluster fragmentation, and collision processes is an accurate description of the potential energy surfaces involved. Up to now accurate potentials have been obtained either by fitting the potential parameters to available high resolution spectroscopic data, providing in this way a local description of the PES, or by performing state-of-the-art electronic structure calculations for numerous configurations to construct a global representation of the surface. The construction of such *ab initio* potentials for polyatomic molecular systems is a complicated and computationally demanding task, and as the number of atoms increases it becomes computationally prohibitive.

Nowadays several surface generation methods have been

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proposed;^{45–48} however, for systems with more than four atoms they do not appear to be competitive as the overall cost associated with fitting procedure and computing the necessary *ab initio* data can be relatively high. In turn, for the traditional fitting methods the main difficulty in constructing a global PES for H_5^+ is the choice of a suitable analytical form to properly reproduce the complicated topology of the surface at short and intermediate ranges, as well as for the anisotropic long-range region. So far, five potential surfaces have been reported in the literature for the H_5^+ , and each of them is based on different theoretical approaches.^{11,17,19,21,23} All these studies are heavily reliant on *ab initio* work, and thus relevant to this article. The first one by Nagashima *et al.*¹¹ is based on a sum of site-site interactions to describe the $H_3^+-H_2$ interaction potential at fixed configurations of the fragments, fitted to MP4 *ab initio* data, while the surface by Kraemer *et al.*¹⁷ has been based on a polynomial functional form in symmetry coordinates fitted to CASSCF/MR-CISD calculations. The next one by Prosmiiti *et al.*¹⁹ has used a first-order diatomics-in-molecules perturbation theory approach to represent the H_5^+ surface without any parametrization to H_5^+ *ab initio* data. The recent ones by Moyano and Collins²¹ and of Xie *et al.*²³ are the more accurate ones. The first one has been constructed by a Shepard-type interpolation on a sparse set of CCSD(T)-MP2 data points, while the second one is based on a generalized many-body expansion that has full permutation symmetry, and has been fitted to 100 000 CCSD(T) *ab initio* points using large basis set. Further, these authors, by using a switching technique, have added to the fitted PES the relevant long-range contributions^{19,23} to extend it. In this way they have obtained a reasonable blended surface containing the long-range interaction. Up to date this latter one is the most accurate global surface for H_5^+ , although the long-range behavior is not adequately described, and the smoothness of the switching still needs to be refined.

Following the tradition in this field, our research should focus on searching a more appropriate functional form than in previous studies, especially for representing the surface in the energy between the intermediate and long-range interactions, and then parametrize it to *ab initio* data available for H_5^+ , and so on. As discussed above, the most accurate surface to date²³ does not properly represent the asymptotes, and so far, there is no interatomic model potential available that is able to describe globally the interactions of the H_5^+ complex. Further, we should also mention that studies of larger species of this series, H_{2n+1}^+ , are more complex. The difficulty in the evaluation of their potential surfaces increases with their size, and high-level calculations are only available on their equilibrium configurations.^{20,49,50} The potential surfaces of all these complexes are expected to be very flat and highly anharmonic, so the task to parametrize the corresponding PESs is laborious even for the H_5^+ one. An alternative way to perform dynamics computations is to carry out direct dynamics trajectory calculations⁵¹ and/or Car–Parrinello⁵² approach for *ab initio* molecular dynamics simulations that combines classical nuclear dynamics calculations with first-principles electronic structure calculations within the density functional theory (DFT) framework.

The purpose of the present study is to use DFT to calculate a surface of H_5^+ . Given the high quality *ab initio* data computed and the available analytical PESs makes H_5^+ especially an attractive target for comparison with the DFT calculations. Thus, here the accuracy of the DFT calculations using different functionals is investigated by analyzing the topology of the PES and compared with high-level CCSD(T) *ab initio* data, as well as with the recent analytical potential surfaces available.^{21,23} To our knowledge several DFT studies on H_{2n+1}^+ systems have been carried out.^{14,53–55} The majority of them have used GGA or hybrid functionals, such as the BLYP and B3LYP (Ref. 56) ones, while in the study by Chermette *et al.*⁵⁷ a new functional, namely B3(H), specially designed for hydrogen-only systems, has been developed and proposed for H_{2n+1}^+ clusters. As we will demonstrate here such B3(H) DFT calculations can describe with sufficient accuracy the H_5^+ surface, including various stationary points on it, as well as at intermediate and long-range configurations, and thus such computations can serve for a global representation of the potential. Such results are of particular interest for studying gas-phase solvation effects, cluster fragmentation, and/or collision processes (in astrophysical applications) following the idea of *ab initio* molecular dynamics simulations.

The plan of this paper is as follows. Section II describes the computational details together with the results obtained from the various DFT calculations. We examine the accuracy of our computations by comparing with CCSD(T) data, and the most recent *ab initio* surfaces for H_5^+ : the one by Moyano and Collins²¹ and the analytical potential by Xie *et al.*²³ Comparisons with previous DFT calculations as well as with the experimental data available are also discussed therein. A summary and some conclusions constitute the closing section.

II. COMPUTATIONAL DETAILS, RESULTS, AND DISCUSSION

All DFT calculations are carried out using GAUSSIAN03 (Ref. 58) and some initial tests are also performed with the Car–Parrinello molecular dynamics (CPMD) package.⁵⁹ First, we carried out geometry optimizations using both G03 and CPMD codes in order to investigate the performance of different basis sets/functionals or pseudopotentials/functionals, respectively. Results on equilibrium energies and configurations from some calculations with cc-pVQZ basis set and different functionals, such as the wide used GGAs (BLYP, BPW91, and PBE),⁶⁰ hybrid-GGAs (B3LYP, B3PW91, and O3LYP),^{56,61,62} and the especially designed for hydrogen-only systems, the B3(H) one,⁵⁷ as well as combination of the GGA functionals with the Vanderbilt’s ultrasoft (VDB) (Ref. 63) and von Barth–Car type (CVB) (Ref. 64) pseudopotentials, as implemented in the CPMD code,⁵⁹ are listed in Table I. Test calculations for the optimized geometry were performed, with and without basis set superposition error (BSSE) correction, by increasing the convergence criterion in the optimization process up to 10^{-12} a.u..

However, for all functionals used, except the B3(H) one, we found an elongated 1- C_{2v} configuration (with the H_2 molecule attached to a substantially distorted H_3^+ unit) almost

TABLE I. Total energies (in a.u.) and bond lengths (in angstrom) of the optimal H_5^+ structure obtained by the present DFT calculations using different functionals/basis sets and their comparisons with those from a previous DFT (Ref. 14) and recent coupled-cluster calculations (Refs. 18 and 19). R_1/R_2 and P are the H–H bond lengths in the H_3^+ and H_2 monomers, respectively, while D is the intermolecular distance between one H atom of H_3^+ and the center of mass of H_2 .

Functional/Basis set	Energy	R_1/R_2	D	P
PBE/cc-pVQZ	−2.528 122 9	1.1434/0.7966	1.0718	0.7966
BPW91/cc-pVQZ	−2.548 186 8	1.1418/0.7923	1.0707	0.7923
BLYP/cc-pVQZ	−2.528 460 1	1.1463/0.7905	1.0760	0.7905
B3PW91/cc-pVQZ	−2.550 283 1	1.1341/0.7890	1.0633	0.7890
O3LYP/cc-pVQZ	−2.546 986 4	1.1336/0.7879	1.0629	0.7879
B3LYP/cc-pVQZ	−2.547 821 8	1.1368/0.7864	1.0667	0.7864
B3(H)/cc-pVQZ($1C_{2v}$)	−2.532 656	0.9967/0.7992	1.2439	0.7611
($2D_{2d}$)	−2.532 512	1.1238/0.7770	1.0545	0.7770
PBE/CVB	−2.525 592	1.1423/0.7949	1.0647	0.7955
GGA/VDB	−2.529 052	1.1447/0.7973	1.0734	0.7972
BLYP/VDB	−2.520 255	1.1486/0.7938	1.0807	0.7935
GGA/CVB ^a	N/A	1.13/...	1.06	0.81
CCSD(T)-R12($1C_{2v}$) ^b	−2.531 794	0.966/0.816	1.324	0.765
($2D_{2d}$) ^b	−2.531 514	1.125/0.780	1.054	0.780
CCSD(T)/cc-pVQZ($1C_{2v}$) ^c	−2.530 509	0.9770/0.8127	1.2918	0.7662
($2D_{2d}$) ^c	−2.530 217	1.1250/0.7849	1.0544	0.7849

^aReference 14.

^bReference 18.

^cReference 19.

indistinguishable in energy with the $2\text{-}D_{2d}$ one (with a proton symmetrically positioned between two H_2 molecules) as an optimal structure for H_5^+ cluster (see bond-length values in Table I). In order to clarify the minimum energy structure, DFT calculations employing larger basis sets, such as aug-cc-pVQZ and aug-cc-pV5Z, were also carried out, and lower total energies of 0.000 01 and 0.000 05 a.u., respectively, were obtained. In Table I we also compare the results of the present DFT calculations with the results of previous DFT ones,¹⁴ as well as with recent CCSD(T) data available.^{18,19}

As shown in Table I the hybrid functionals yield lower energy results and shorter bond length and intermolecular distances than GGA ones, being in closer agreement to the previous CCSD(T) calculations. According to those results, as we mentioned above, the $1\text{-}C_{2v}$ structure has the lowest energy followed by the $2\text{-}D_{2d}$ one, where the proton is situated in the middle of the two hydrogen molecules and corresponds to the saddle-point for the proton transfer. The energy difference between these two structures has been predicted by CCSD(T)[DTQ]/CBS calculations to be only 0.20 kcal/mol.²⁰ As we can see here all DFT calculations fail to reproduce them, and only the ones employing the B3(H) functional can distinguish between these two configurations. The B3(H) DFT calculations predict an energy difference of 0.09 kcal/mol between the $1\text{-}C_{2v}$ and $2\text{-}D_{2d}$ structures. Also by comparing the optimized geometries of the DFT computations we found that the ones obtained from the B3(H)/cc-pVQZ calculations are in excellent agreement with the CC-R12 and CCSD(T) results.^{18,20}

In Fig. 1 we plot the minimum total energy path between these two conformers at different levels of theory, such as HF, MP2, CCSD(T) together with the results of B3(H), B3LYP, and B3PW91 using cc-pVQZ basis set, as well as the curve obtained from the recent CCSD(T)/aug-cc-pVTZ

parametrized surface.²³ The distance between the centers of mass of the two H_2 molecules is fixed in their equilibrium value of the $2\text{-}D_{2d}$ configuration of H_5^+ , while the X-axis shows the position of the central proton between them. The total energy is calculated by optimizing the H_5^+ geometry for each point of the X-axis at the specific level of theory. The HF approach predicts a higher barrier of ≈ 1.5 kcal/mol than

FIG. 1. Total energies for H_5^+ obtained at indicated levels using cc-pVQZ basis set, together with the ones obtained for the analytical surface from Ref. 23. The X-axis shows the position of the central proton between the two H_2 monomers, which are fixed at the $2\text{-}D_{2d}$ configuration of H_5^+ .

TABLE II. Harmonic vibrational frequencies (in cm^{-1}) for 1- C_{2v} /2- D_{2d} conformers of H_3^+ calculated in the present work (DFT) and comparison with previous benchmark results. The number of the negative values indicates the order of the saddle-point.

Mode	This work						CCSD(T) ^a	PES ^b
	PBE	BLYP	BPW91	B3LYP	B3PW91	B3(H)		
1	227	223	226	228	230	204/−449	206/−531	211/−503
2	870	674	841	534	705	607/234	495/224	487/217
3	895	890	900	922	927	796/965	812/962	829/971
4	895	890	900	922	927	890/965	866/962	882/971
5	1346	1324	1347	1363	1379	1211/1412	1170/1411	1190/1430
6	1464	1422	1462	1500	1529	1878/1610	1838/1593	1799/1616
7	1464	1422	1462	1500	1529	2165/1610	2131/1593	2128/1616
8	3770	3804	3797	3869	3858	3815/3989	3668/3892	3666/3861
9	3849	3883	3875	3951	3939	4203/4077	4115/3965	4091/3924

^aReference 20.

^bReference 23.

the MP2 and CCSD(T) correlated methods, where a lower barrier of ≈ 0.2 kcal/mol is obtained between the two wells. The B3(H) functional yields a double well topology very similar to the CCSD(T) one, while all others used here, e.g., the B3LYP and B3PW91, predict a symmetric structure with a single very flat potential well. We thus conclude that the B3(H) functional represents pretty accurately this energy path in contrast to the B3LYP and B3PW91 ones.

Further, and in order to analyze the character of the optimal structure, we carried out harmonic frequency calculations at the above mentioned stationary points of the potential surface. The results of this normal-mode analysis are given in Table II. As seen all GGAs or hybrid functional DFT calculations predict an elongated 1- C_{2v} structure to be the energetically lowest stationary point, and is the minimum

on the H_3^+ surface with very similar normal-mode frequencies. However, among the different functionals again only the B3(H) one predicts the existence of the 2- D_{2d} structure as a first-order saddle-point, with the calculated harmonic frequencies to be in very good agreement with those from previous benchmark calculations,²⁰ as well as with the ones from the recent analytical PES.²³

A more detailed and quantitative insight into the bonding may be obtained from the comparison of total and correlation energies for a specific configuration. In Table III we present such results for the optimized H_3^+ structure at B3LYP/cc-pVQZ level for all DFT and the CCSD(T)/cc-pVQZ calculations, and the optimized geometry at CCSD(T)/aug-cc-pVQZ one for the coupled-cluster ones. Correlation energies are computed using accordingly the exchange-correlation

TABLE III. Total and correlation energies (in a.u.) of optimized H_3^+ structures, obtained at B3LYP/cc-pVQZ and CCSD(T)/aug-cc-pVQZ levels of theory, and extrapolation of the coupled-cluster values to their CBS limit.

Geometry	Method/Basis set	E_{tot}	ΔE_{cor}
Optimized B3LYP/cc-pVQZ	BPW91/cc-pVQZ	−2.548 136 7	−0.101 728 3 ^a
	BLYP/cc-pVQZ	−2.528 407 6	−0.081 999 2 ^a
	B3PW91/cc-pVQZ	−2.550 271 5	−0.110 107 8 ^b
	B3LYP/cc-pVQZ	−2.547 821 8	−0.107 758 1 ^b
	B3(H)/cc-pVQZ	−2.532 351 5	−0.092 287 8 ^b
	CCSD(T)/cc-pVQZ	−2.530 133 0	−0.090 069 3 ^b
Optimized CCSD(T)/aug-cc-pVQZ	CCSD(T)/aug-cc-pVQZ	−2.530 697 1	−0.088 964 1
	CCSD(T)/AV5Z	−2.531 510 4	−0.089 465 8
	CCSD(T)/AV6Z	−2.531 735 3	−0.089 653 2
	CCSD(T)/CBS[Q56] ^c	−2.531 866 0	−0.089 766 0 ^d
	CCSD(T)/CBS[56] ^e	−2.531 992 7	−0.089 910 6
	CCSD(T)/cc-pV8Z	−2.531 837 3	−0.089 748 4
	CCSD(TQ)/aug-cc-pVQZ	−2.530 776 6	−0.089 043 6
	CCSD(TQ)/CBS[56] ^f	−2.532 072 2	−0.089 990 1
	Literature ^g	−2.5320	−0.089 559

^aCorrelation values were obtained as the difference from the HFB/cc-pVQZ energy (HF=−2.446 408 4 a.u.).

^bCorrelation values were calculated by the difference with the HF/cc-pVQZ energy (HF=−2.440 063 7 a.u.).

^cReference 65.

^dThe correlation energy was obtained by the difference of CCSD(T)/CBS[Q56] and HF/CBS[Q56] energies.

^eReference 66.

^fThese values were calculated including the contribution of quadruple excitations at CCSD(TQ)/aug-cc-pVQZ level to the CCSD(T)/CBS (Ref. 56) extrapolation value.

^gReference 18.

TABLE IV. Total energy (in a.u.) for the 1-C_{2v} global minimum structure and relative energies (in kcal/mol) for the indicated H₅⁺ optimized conformers predicted by the present DFT calculations and compared with previous ones.

Conformer	This work			CCSD(T)-R12 ^a	QCISD(T) ^b	PES ^c	PES ^d
	B3PW91	B3LYP	B3(H)				
1C _{2v}	-2.550 283	-2.547 822	-2.532 656	-2.531 794	-2.530 509	-2.518 215	-2.528 015
2D _{2d}	0.000	0.000	0.090	0.176	0.183	0.080	0.149
3C _{2v}	0.339	0.349	0.302	0.276	0.273	0.256	0.295
4D _{2h}	0.339	0.349	0.483	0.521	0.520	0.419	0.458
5C _{2v}	7.377	8.235	5.075	...	4.413	5.635	4.477
6C _{2v}	7.923	8.779	7.021	...	6.573	6.076	6.886
7C _{2v}	7.764	8.650	5.455	...	4.781	5.687	4.795
8C _{2v}	10.769	11.569	8.384	...	7.615	7.139	7.144
9C _s	10.058	10.916	7.198	...	6.208	7.264	6.022
10C _{3v}	11.792	12.621	9.105	...	8.104	8.011	7.756

^aReference 18.

^bReference 19.

^cReference 21.

^dReference 23.

functionals for the GGA-type calculations, while for the hybrid functionals, as well as for the CC ones, their values are estimated by the difference of the corresponding HF energies. Further, extrapolation schemes to converge energies to the (approximate) complete basis set (CBS) limit are employed. In particular, we utilized one of the most widely used, the mixed Gaussian/exponential three-point form proposed by Peterson *et al.*,⁶⁵ $E_X = E_{\text{CBS}} + Ae^{-(X-1)} + Be^{-(X-1)^2}$, where X is the cardinal number, in the series of aug-cc-pVQZ, aug-cc-pV5Z, and aug-cc-pV6Z basis sets, and the two-point single inverse power function first introduced by Schwartz⁶⁶ for the correlation energies, $E_X = E_{\text{CBS}} + A/X^3$, assuming the aug-cc-pV5Z and aug-cc-pV6Z basis sets. Table III also shows the results from CCSD(TQ) calculations and in current case an estimate of nearly 0.000 08 a.u. (0.05 kcal/mol) was obtained for the contribution of quadruplet substitutions with the aug-cc-pVQZ basis set to the correlation energy. Taken into account this contribution a correlation energy of about 0.089 99 a.u. is predicted by the CCSD(TQ)/CBS (Ref. 56) computations. On the other hand, from the DFT calculations somewhat higher correlation energy is estimated for the B3LYP/cc-pVQZ optimized structure, and as we can see the PW91 correlation functional overestimates the correlation energy compared to the LYP one. Further, as it was expected, the values obtained with the B3(H) functional (0.0923 a.u.) are more close to the CCSD(TQ) results (0.090 a.u.) than the B3LYP one, which counts for 0.108 a.u. (see Table III). We should mention here that B3LYP functional has been parametrized for the G2 set of molecules,⁵⁶ while the latter functional has been designed for hydrogen-only systems. Chermette *et al.*⁵⁷ fitted the B3LYP functional parameters of pure exchange, gradient-corrected exchange, and gradient-corrected correlation terms to the equilibrium geometrical data of H₅⁺ at CCSD(T) level of theory, whereas CCSD(T) data for H₃⁺ and larger clusters up to H₉⁺ have been used to evaluate the efficiency of the fit. Such parametrization has led to the B3(H) hybrid functional which includes a larger amount of pure exchange than the B3LYP one, al-

though it has been found⁵⁷ reasonable for hydrogen-only systems, and certainly the most important term for the long-range interactions.

In order now to further check the accuracy of the hybrid functionals we locate the ten stationary points on the H₅⁺ surface, reported by Yamaguchi *et al.*¹⁰ The results of the present calculations for the optimized structures are summarized in Table IV, together with the comparisons with data of previous high-level *ab initio* calculations^{18,19} and the recent analytical potential surfaces.^{21,23} Once again the calculations based on B3(H) functional reproduce remarkably well all ten stationary points predicted by Yamaguchi *et al.*¹⁰ (we keep the designation introduced by these authors), and the optimal structures at the B3(H)/cc-pVQZ level for them are depicted in Fig. 2. As we can see B3PW91 and B3LYP functionals failed in reproducing the difference between the no-planar 1-C_{2v} and 2-D_{2d} conformers, as well as the planar 3-C_{2v} and 4-D_{2h} ones. Compared to the CCSD(T) data we see that small changes are predicted in geometry and in total energy of all stationary points from the B3(H) DFT calculations, although the order and energy separation of these conformers are very close to the CCSD(T) ones.^{18-21,23} The first four low-lying configurations (1-4) are very close to each other in energy within 0.483 a.u. for the B3(H)/cc-pVQZ compared to 0.521 a.u. for the CCSD(T)-R12 (Ref. 18) results, while the energy difference of the first two conformers is predicted to be 0.09 kcal/mol, that is lower than the CCSD(T) one (0.176 kcal/mol), although very similar to one of the MP2 surface by Moyano and Collins.²¹ As it can be seen the energy separation for the configurations of the second group (5-10) predicted from the B3(H) calculations is 5.075 kcal/mol, that is between the CCSD(T) and MP2 data,^{20,21,23} while the other two functionals, B3PW91 and B3LYP, predict somehow higher difference of 8.235 and 7.377 kcal/mol, respectively. All functionals used predict the same relative order within these structures that is different to the one from the CCSD(T) calculations. From the B3(H) calculations a lower relative energy is obtained for the 6-C_{2v} compared to the 9-C_s one, in agreement with the MP2 surface,²¹ and in

FIG. 2. Structures of the ten low-lying stationary points on H_3^+ surface obtained at B3(H)/cc-pVQZ level of theory.

contrast to the CCSD(T) estimations. However, we should note that the relative energies obtained with the B3(H) functional for these conformers are much closer to the CCSD(T) ones than the ones estimated from the other two functionals. Based now on the Hessian analysis of the harmonic frequencies at B3(H)/cc-pVQZ level, among the ten conformers the $1-C_{2v}$ is the only minimum, while the next ones are saddle-points of the surface of the following order: first for the $2-D_{2d}$, $3-C_{2v}$, and $5-C_{2v}$, second for the $4-D_{2h}$, $6-C_{2v}$, $7-C_{2v}$, and $9-C_s$, third for $8-C_{2v}$, and fourth for the $10-C_{3v}$. This is in absolute agreement with the QCISD(T) results.¹⁹

As already stated, H_3^+ cluster can be described as a distorted H_3^+ nucleus weakly linked to an H_2 molecule, and a first dissociation reaction would be a loss of the H_2 molecule. In order to carry out reaction or photofragmentation dynamics calculations the surface should correctly describe both the short-range, intermediate, as well as long-range features of the H_3^+ . Therefore, we performed a series of calculations at various intermolecular distances and relative orientations of H_3^+ and H_2 to represent a description of the most important intermolecular interactions between the two monomers. The relative orientations of the H_3^+ and H_2 are chosen according to the $1-C_{2v}$, $3-C_{2v}$, $5-C_{2v}$, $7-C_{2v}$, $9-C_s$, $6-C_{2v}$, $8-C_{2v}$, and $10-C_{3v}$ low-lying structures, which are displayed in Fig. 2.

FIG. 3. Interaction energies for $H_3^+ \cdots H_2$ (in kcal/mol) as a function of the intermolecular distance R connecting the centers of mass of H_3^+ and H_2 monomers in their equilibrium configurations obtained by CCSD(T)/cc-pVQZ and B3(H)/cc-pVQZ calculations, together with the values of the analytical surface from Ref. 23. The relative orientations for the two monomers (indicated in each panel) are chosen from the ten conformers of H_3^+ (see Fig. 2).

The H_3^+ and H_2 are fixed to their equilibrium geometries at CCSD(T) level, while the intermolecular distance R between their center of masses is varied from 1.5 to 20 Å. As we show above, the B3(H) functional provides the most reliable description of the H_3^+ potential, and thus here we only consider it to compare with the CCSD(T) data. The results of the B3(H)/cc-pVQZ and CCSD(T)/cc-pVQZ calculations together with their comparison with the ones obtained from the recent analytical PES by Xie *et al.*²³ are presented in Fig. 3. The interaction energies are relative to the $H_3^+ + H_2$ dissociation limit for each level of calculation. One can see that the B3(H) curves are in very good accord with the CCSD(T) ones, particularly for the intermediate and long-range interactions, while in the short-range regime small deviations are found. The largest difference is obtained for the $1-C_{2v}$ and $3-C_{2v}$ orientations, where the B3(H) predicts more stable structures by an energy of 0.6 kcal/mol compared to the corresponding CCSD(T) data. Also deeper well-depths are found for the $6-C_{2v}$, $8-C_{2v}$, $5-C_{2v}$, and $7-C_{2v}$ conformers, whereas for the $9-C_s$ and $10-C_{3v}$ the B3(H) and CCSD(T) results are in excellent agreement. In general, for all points in Fig. 3 and for the energy range from -7 to 4 kcal/mol a mean absolute error (MAE) of 0.16 kcal/mol is obtained between the B3(H) interaction energies and the CCSD(T) ones. Compared now with the curves obtained from the recent analytical CCSD(T) parametrized PES by Xie *et al.*²³ one can see significant differences in the intermediate and long-range regions for all configurations studied, and in particular for the $6-C_{2v}$, $8-C_{2v}$, $9-C_s$, and $10-C_{3v}$ ones, where these deviations are large even in the short-range area. As discussed previously by Prosimi *et al.*¹⁹ the short-range forces for chemical binding are small, although considerable for the above mentioned structures, e.g., $9-C_s$ one, and also the relevant long-range interaction, mainly the charge-induced dipole and the charge-quadrupole terms, behaves differently depending on how H_2 approaches a corner (cases 1, 3, and

FIG. 4. Mean absolute error for the B3(H) and CCSD(T) interaction energies as a function of the CCSD(T) ones obtained (a) for a fixed energy range of 1 kcal/mol, (b) for a fixed number of 1000 data points, and (c) as a function of the number of points below each energy.

6), or a side (5, 7, and 8) or the center (9 and 10) of the H_3^+ . We should note that the “artifact” for the intermediate to large intermolecular distances of the analytical PES seems that it may be attributed to the smoothness of the switching procedure adopted by Xie *et al.*²³ in order to represent correctly the long-range interactions.

In Fig. 4 we present the relation between the MAE in the interaction energies obtained from B3(H) and CCSD(T) calculations using the cc-pVQZ basis set as a function to the CCSD(T) interaction energy relative to the $\text{H}_3^+ + \text{H}_2$ dissociation. We choose to calculate the B3(H) and CCSD(T) energies at 30521 configurations of the H_5^+ to explore different energy regimes. As the distribution of the data points is not uniform with the energy, the mean absolute error values between the B3(H) and CCSD(T) interaction energy values are estimated for both fixed energy range of 1 kcal/mol [see Fig. 4(a)] as well as for a fixed number of 1000 points [see Fig. 4(b)]. Also the cumulative mean absolute error value by increasing the number of data points is obtained and plotted [see Fig. 4(c)]. As we can see the MAE error is smaller at low energies, about 0.3 kcal/mol, and increases up to 0.8 kcal/mol for energies near the dissociation limit of $\text{H}_3^+ + \text{H}_2$, where a higher number of data was available. The total MAE error for all negative energy points is 0.47 kcal/mol, and for all positive energy ones 0.62 kcal/mol, while a value of 0.54 kcal/mol is obtained for the whole data set. As we have mentioned above, B3(H) calculations predict lower interaction energies than the CCSD(T) with somehow larger deviation from the CCSD(T) ones for the energies of dissociative configurations. However, we should mention that such approach provides a global, realistic, and computationally feasible representation of the H_5^+ surface.

Two-dimensional contour plots of the potential B3(H) DFT surface are shown in Fig. 5, where we choose different

FIG. 5. Contour plots of the B3(H)/cc-pVQZ surface of the H_5^+ . In the inset of each panel the corresponding relative orientation for the H_3^+ and H_2 monomers to 1- C_{2v} , 7- C_{2v} , and 9- C_s (from top to bottom panel) of H_5^+ is also shown. Contour lines are plotted for the energy ranges: -9.0 to 9.0 kcal/mol with an interval of 3.0 kcal/mol (top panel), -9.5 to -9.0 kcal/mol and -9.0 to 8.0 kcal/mol with intervals of 0.1 and 0.5 kcal/mol, respectively (first middle panel), -7.0 to 0.0 kcal/mol and 0.0 – 10.0 kcal/mol with intervals of 1.0 and 5.0 kcal/mol, respectively (second middle panel), -7.0 to 0.0 kcal/mol and 0.0 – 10.0 kcal/mol with steps of 0.1 and 5 kcal/mol, respectively (bottom panel).

orientations of the H_3^+ to provide an overall picture of the interaction. The representation of the PES is displayed in four plots. They show projections of the interaction energy for three different fixed configurations of H_5^+ , corresponding to 1- C_{2v} (see top and first middle panels of Fig. 5), 7- C_{2v} (see second middle panel of Fig. 5), and 9- C_s (see bottom panel of Fig. 5) ones. These configurations are also indicated in the inset of Fig. 5. One H atom of the H_3^+ is positioned at

the origin of the coordinate system, and its three H atoms are placed in the XY-plane. R' , θ , and ϕ are the spherical coordinates of the center of mass of H_2 with respect to the fixed origin, while D and $R_1/R_2/R_3$ are the intermolecular distance between the fixed H atom and the center of mass of H_2 , and the HH bond lengths in the H_3^+ , as they were defined above (see Table I). In the top and first middle panels the equipotential curves are shown in the (D, R_1) with $R_1=R_3$ and (D, θ) coordinates, respectively, with H_5^+ fixed at 1- C_{2v} orientation. The contours of the surface are demonstrated around the global minimum, as well as the area nearby the planar 3- C_{2v} saddle-point between the two symmetric no-planar 1- C_{2v} conformers. One can see the flatness of the potential around the minimum, as well as the dissociation channels to $H_3^+ + H_2$ in D and $R_1=R_3$ coordinates. In the second middle panel contour lines are plotted in the (D, ϕ) plane with the H_5 fixed in 7- C_{2v} geometry. The details of the surface around the 3- C_{2v} and 6- C_{2v} as well as for the 7- C_{2v} and 8- C_{2v} stationary points are shown. As we mentioned above 3- C_{2v} is first-order saddle-point, while 6- C_{2v} and 7- C_{2v} are second order ones, and 8- C_{2v} a third order one. In turn, in the bottom panel of Fig. 5 the PES around the 9- C_s geometry (third order saddle-point) is presented together with the nearby 10- C_{3v} (fourth order saddle-point) one. As one can expect these differences in the order of the saddle-points appear in the plots.

In the following we will discuss the stability of H_5^+ by determining its dissociation energy, as well as the enthalpy variation for the $H_5^+ \rightarrow H_3^+ + H_2$ given by

$$\Delta H = [H_{(H_3^+)} + H_{H_2}] - H_{H_5^+} \quad (1)$$

or

$$\Delta H = -D_e + \Delta(ZPVE) + \Delta(\epsilon(T)),$$

where H are the enthalpies for H_2 , H_3^+ , and H_5^+ given by $H^{298.15} = E + ZPVE + \epsilon(T)$, $D_e = E(H_3^+) - [E(H_3) + E(H_2)] + E_{BSSE}$, ZPVE are the zero-point vibrational energy corrections, and $\epsilon(T)$ are the thermal corrections, accounting the effects of molecular translation, vibration, and rotation at specific temperature and pressure⁶⁷ for H_2 , H_3^+ , and H_5^+ obtained from the optimization B3(H)/cc-pVQZ calculations.

By considering the results of the harmonic vibrational frequency analysis, zero-point vibrational energy, as well as thermal corrections for both reactants and products, the dissociation energies including ZPVE, D_0 , and enthalpy variation $-\Delta H$ for the equilibria clustering $H_3^+ + H_2 \rightleftharpoons H_5^+$ reaction were obtained. In Table V we present the calculated values of the present study and compared them with the ones from previous theoretical calculations,^{14–16,18,20,21,23,27} as well as various experimental measurements.^{28–31,33,37–39} As we can see in Table V the predicted D_e and D_0 energies computed here by the DFT calculations are varied from 13.30 and 11.03 kcal/mol using the BLYP to 9.47 and 6.79 kcal/mol with the B3(H) functional, respectively. The results obtained by B3(H) are in fairly good agreement with those obtained by CC studies.^{18,20} Whereas the B3(H) values are somewhat higher by 0.8–0.9 kcal/mol, compared with the ones obtained by previous CC-R12 and CCSD(T) studies,^{18,20} the deviations become 3.6, 4.2, and 4.7 kcal/mol, respectively, for

TABLE V. Theoretical dissociation energies D_e and D_0 (in kcal/mol) for H_5^+ , together with enthalpy variations obtained in the present DFT calculations, as well as in previous studies and compared with experimental values of dissociation enthalpies for $H_5^+ \rightarrow H_3^+ + H_2$.

Theory or Expt.	D_e	$\Delta(ZPVE)$	D_0	ΔH (153/298.15 K)
BLYP/cc-pVQZ	13.30	2.27	11.03	11.41/11.70
B3PW91/cc-pVQZ	12.80	2.53	10.27	10.91/11.20
B3LYP/cc-pVQZ	12.23	2.22	10.01	10.40/10.69
B3(H)/cc-pVQZ(1C _{2v})	9.47	2.68	6.79	7.64/7.93
B3(H)/cc-pVQZ(2D _{2d})	9.38		6.70	7.55/7.84
DFT ^a			14.5	
G2(MP2) ^b	8.90			6.20/...
MP4 ^c	7.84			6.91/...
CC-R12 ^d	8.58	2.48	6.09	
CCSD(T) ^e	8.65	2.74	5.91	7.10/7.39
MP2 ^f	7.70	...	5.00	
CC-PES ^g	8.30	2.73	5.57	
CC-PES/DMC ^h	8.30	...	6.37	
Ref. 37				5.1 ± 1.2
Ref. 28				9.7
Ref. 29				9.6
Ref. 38				8.1 ± 0.1
Ref. 39				5.8 ± 1.2
Ref. 30				6.6 ± 0.3
Ref. 31				6.9 ± 0.3
Ref. 33				7.0 ± 0.1
Ref. 35				<7.44

^aReference 14.

^bReference 15.

^cReference 16.

^dReference 18.

^eReference 20.

^fReference 21.

^gReference 23.

^hReference 27.

B3LYP, B3PW91, and BLYP functionals. These DFT calculations predict a stronger bound H_5^+ complex than the CC ones, and as we have mentioned above only one, the 2- D_{2d} , a very flat potential well. In contrast, we should note that the MP2 calculations²¹ underestimate the binding energies by 0.9 kcal/mol, that is the same factor with the B3(H) ones compared to the CC data. Also we present a comparison with the latest data for the D_0 value predicted by diffusion Monte Carlo calculations employing the surface by Xie *et al.*²³ In this latter study by including correctly the anharmonicities of the surface, a D_0 value of 6.37 kcal/mol has been predicted; however, the zero-point averaged structure of H_5^+ has been found to be of the D_{2d} geometry.²⁷ Given that the energy difference between the 1- C_{2v} and 2- D_{2d} is only 0.09 kcal/mol at B3(H) calculations, we also list in Table V a D_0 value within the harmonic approximation for the 2- D_{2d} configuration of 6.70 kcal/mol. The only experimental data available on the D_0 energy for the H_5^+ have been reported recently by Cheng *et al.*³⁵ The authors based on the lower-energy band at 2603 cm⁻¹ in the recorded IR spectrum of H_5^+ have established a firm upper limit corresponding to 7.44 kcal/mol. This value is consistent, and very close to the one predicted by the harmonic B3(H) estimate, although is slightly higher than all theoretical predicted ones (see Table V).

Further, in order to compare with more experimental data the computed enthalpy variation values $-\Delta H$ are listed in the last column of Table V. Several experimental data are available for the clustering reaction over the range of tem-

perature of 25–300 K.^{28–31,33,37–39} The enthalpy variation values are temperature dependent, and generally increase as temperature increases. Therefore, for a direct comparison with the most recent experimental data (see van't Hoff plots in Refs. 30, 31, and 33), $-\Delta H$ values are given for 298.15 K, and also for comparison with previous calculations, for 153 K. Once again the BLYP, B3PW91, and B3LYP calculations provide enthalpy values in poor agreement with the experimental data. These DFT values are high enough compared to experimental data with deviations of 67%–48%. Such significant differences emphasize the inaccuracy of the corresponding DFT calculations. On the other hand the B3(H) results predict an enthalpy variation value of 7.93 and 7.64 kcal/mol at 298.15 and 153 K, respectively, that is consistent with the MP2, MP4, and CCSD(T) ones. By comparing these values with the experimental ones,^{30,31,33} we found a deviation of 10%, suggesting that B3(H) calculations can quantitatively describe the H_5^+ system.

III. SUMMARY AND CONCLUSIONS

We presented a potential energy surface by performing DFT calculations at a large number of geometries for the H_5^+ cluster. Different GGA and hybrid functionals were used and their efficiency to treat the energetics of the weak bonds that are present in the H_5^+ cluster was checked. In this way equilibrium structures as well as the features of intermolecular interaction at intermediate and long distances were investigated. Among all functionals studied, a hybrid one, namely, B3(H), which has been specially designed for the description of hydrogen-only systems, was found to be able to recover with remarkable accuracy the main features on the H_5^+ surface. Our results were compared with the most accurate to date analytical CCSD(T) potential surface, previous high level CC-R12 and CCSD(T) calculations, as well as with CCSD(T) additional reference computations carried out here for this purpose. We found that with this functional the calculated surface has the appropriate topology to describe with very good accuracy and low computational cost all aspects of the interaction H_5^+ potential, such as the known ten lower stationary points, including the transition state for the proton transfer between the two H_2 molecules, as well as the correct asymptotic behavior of the long-range electrostatic interactions for all configurations studied. Such description is important for studying the role of this ion-molecule complex in the mechanisms of collision or fragmentation reactions, with a particular interest at low temperatures due to its relevance in astrophysical applications.

Further, total interaction energies and normal frequencies for these conformers were obtained and show a good accord with benchmark results. A more quantitative insight into bonding was obtained from the comparison of the theoretical values of dissociation energies and measured dissociation enthalpies. The dissociation energies and enthalpy variations for the equilibrium $H_3^+ + H_2 \rightleftharpoons H_5^+$ reaction were estimated for the B3(H)/cc-pVQZ calculations and compared with previous theoretical predictions, as well as with various, earlier and recent, experimental data available. In general the values obtained from the B3(H)/cc-pVQZ computations pre-

dict a more tighter C_{2v} structure for the H_5^+ , and compare very well with benchmark CCSD(T) results. The present B3(H) DFT data are also found in a very good quantitative agreement with the most recent experimental data.

Even though significant progress has been recently made on the potential surface calculation of H_5^+ we think that there is still room for further improvement. In one hand, the accuracy of the present DFT approach in representing the H_5^+ surface was confirmed by more extensive comparisons with high level CCSD(T) calculations. Based on these data we report a total MAE value of 0.5 kcal/mol for energies up to 6 kcal/mol for the whole set of data, with slightly larger deviations especially in regions corresponding to dissociative configurations. On the other hand, comparison with previous analytical CCSD(T) surface shows that improvements are needed in the functional form for the asymptotic regions,⁶⁸ and a global parametrized analytical potential for H_5^+ still remains a challenge. Therefore, studies in both directions, such as traditional analytical fitting procedures,⁶⁸ as well as improved parametrized DFT functionals, are necessary if progress is to be made on the open questions on the H_5^+ dynamics.

Further, this work underlines the interest in determining accurate potential energy surfaces within the DFT framework for the protonated hydrogen clusters. In case of H_5^+ we show that such approach yields a reliable interaction potential, and thus first-principles dynamics calculations can be carried out to study the spectroscopy, collision, and/or fragmentation dynamics of the system.⁶⁹ In fact, the H_5^+ can be regarded as the simplest system including internal proton transfer, and therefore the investigation of its molecular properties is an important step to understand larger complexes. Accordingly, one expects that reasonable description of energetics, low-lying structures, and dissociation asymptotes will be possible using such functional for larger H_n^+ clusters. It would be interesting to see if larger sizes of these clusters confirm this picture. Work in these directions is in progress.

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