Structure and energetics of H_{15}^+ hydrogen clusters

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Low-lying stationary points on the H_{15}^+ potential energy hypersurface have been determined through Hartree-Fock (HF) calculations and density functional theory (DFT) with the recently proposed functional especially designed for hydrogen systems [$B3(H)$]. Calculations have been carried out for three conformers of H_{15}^+ ($C3v$,Cs, and $D3h$ symmetries) leading to fully optimized structures and energies. Only the $C3v$ and Cs structures are true minima. The total energy of the Cs structure lies 10^{-4} Hartrees lower than the $C3v$ one. Vibrational frequencies and infrared intensities for both stationnary points have been predicted within HF and DFT $B3(H)$ methods. [S0163-1829(99)12029-0]

I. INTRODUCTION

Ionic clusters such as $H_3^+(H_2)_n$ are important species in the stratosphere,[1] where molecules readily nucleate about ions as a result of the long-range attractive forces dominating ion-molecule interactions. Such weakly bound molecular cluster ions have thus attracted much attention. Clampitt and Gowland[2] observed H_5^+ up to H_{47}^+ odd-numbered clusters by sweeping a low-energy electron beam over a condensed H_2 surface. Their initial mass distribution showed H_{15}^+ to be one of the most abundant ions. For this H_{15}^+ ion, they proposed an octahedral structure of the general form $H_3^+(H_2)_n$. Van Lumig and Reuss[3] measured the dissociation cross section of hydrogen clusters with He target in the projectile kinetic energy range. They suggested the existence of particularly stable H_9^+, H_{15}^+, H_{19}^+, and H_{23}^+. The gas-phase clustering reaction $H_3^+(H_2)_{n-1}+H_2 \rightarrow H_3^+(H_2)_n$ has been studied by several investigators.[4] Hiraoka and Mori[4] have studied the thermochemical properties and stabilities of $H_3^+(H_2)_n$ clusters and suggested a successive shell formation for the clusters $H_3^+(H_2)_n$ with $n=3$, 6, 8, and 10. Bae and co-workers[5] have also observed shell formation for the clusters $H_3^+(H_2)_n$ sequentially grown on seed positive ions generated by electron impact ionization in a pulsed supersonic jet. They suggested a pentagonal bipyramid structure for the H_{15}^+ ionic cluster. The H_{15}^+ system is of special interest since it has often been experimentally observed to possess a relatively high stability.

Theoretical descriptions of the smallest clusters of the H_{2n+1}^+ family have been given at various levels of theory. They belong either to the *ab initio* [Hartree-Fock (HF) and post-HF] models, or the density functional theory (DFT) approach. This last case includes both Kohn-Sham (KS) (Ref. 6) and Car-Parrinello (CP) calculations.[7] The structure of the $H_3^+(H_2)_n$ clusters are generally described as H_2 units surrounding an H_3^+ core. These clusters are very weakly bounded and require fairly large basis sets for covering results. To our knowledge, only one *ab initio* calculation has been performed yet beyond H_{13}^+ by Diekmann *et al.*[8]

In a recent paper,[9] Stich *et al.* carried out a quantum simulation bearing on H_3^+, H_5^+, H_7^+, H_9^+, and H_{27}^+. Their Car-Parrinello calculations showed that the H_2 molecules constituting the solvation shells around the tightly localized H_3^+ core are weakly bonded. This feature affects mostly the rotations of the solvating H_2 in what they called a ''quantum plasticity'' since classical simulations would lead to more rigid clusters.[9,10] These conclusions are in good agreement with the flat potential energy surface (PES) we obtain through the geometry optimizations processes performed in the present work and previous calculations.[11–13] However Stich *et al.*[9] used for their dynamics forces calculations within Kohn-Sham DFT formalism using the PW91 (Ref. 15) exchange-correlation functional. Although they claimed that the structures they obtained agree within 5% on average with our reference structures (and even within less than 3% for the largest clusters, probably H_{11}^+–H_{13}^+), this hides large deviations for the smallest clusters, namely, H_5^+ and H_7^+.[10] Indeed, we have shown[11] that any popular DFT functional (GGAs, B3LYP, . . .) of the time being are unable to describe properly H_5^+.

The aim of this paper is to describe the properties and structure of the H_{15}^+ ion which has been claimed in the past to be especially stable. For this purpose because the HF method is known to be insufficiently accurate to describe properly weakly bonded or highly correlated systems, we have recently performed calculations using a DFT functional

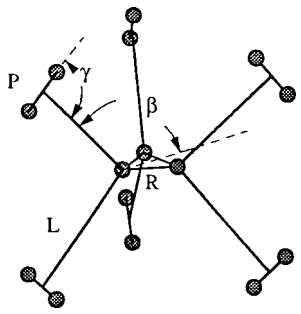

FIG. 1. H_{15}^{+} optimized structure in $D3h$ symmetry.

especially designed for such systems [named $B3(H)$].[11] We report here on theoretical prediction of the structures and energies of three conformers of H_{15}^{+} with Cs, $C3v$, and $D3h$ symmetries. The corresponding vibrational frequencies (calculated within the harmonic approximation) and infrared intensities are also given. Some concluding remarks will be given bearing on the adequacy of both HF and DFT models [with the $B3(H)$ functional] for the description of hydrogenic clusters.

II. THEORETICAL APPROACH

In previous theoretical studies,[12,13] *ab initio* self-consistent-field Hartree-Fock (SCF) and configuration interaction (CI) calculations have been carried out for $H_3^{+}(H_2)_n$ $(n=1-5)$ clusters using a triple-zeta plus polarization basis set. Especially, we found that the structures of H_{11}^{+} and H_{13}^{+} clusters[13] can be viewed as resulting of the addition of H_2 molecules to a weakly deformed H_9^{+} core. Because the computational effort increases as n^6 for CISD calculations (which are not size consistent), n^7 for CCSD(T) (n being the size of the basis set which is proportional to the number of atoms), some of us developed recently a density functional which allows one to tackle the hydrogen clusters problem within DFT.[11] In DFT the computational effort scales formally as n^3 for LDA or GGA approximations and n^4 for hybrid functionals which contain some HF exchange. Indeed, with efficient codes, the computational effort can be reduced up to $n^{2.7}$, thanks to cutoffs for integral computations.

This functional named $B3(H)$ has been proved to lead to geometries and energies of H_{2n+3}^{+} clusters which are close to those obtain through CCSD(T) calculations, which for these kind of species are not very different to CISD ones. The parametrization of the $B3(H)$ functional was fitted on H_5^{+} structure, and found adequate for all clusters sizes from H_3^{+} to H_{13}^{+}.[11]

In the present work , we extend our work of characterization of H_{2n+3}^{+} species to the H_{15}^{+} ion. The computations were performed with the Gaussian 94 package.[16] The H_{15}^{+} cluster structure has been computed at three levels of theory, HF, CISD, and DFT/$B3(H)$. In a previous paper,[11] we have studied the accuracy of the basis sets and found that the 6-311G** (unfortunately misprinted ++ in Ref. 11) was satisfactory for this kind of systems. This basis set has been retained as well in Farizon *et al.*, post Hartree-Fock work.[12] In order to test the quality of this basis set for bigger systems, which could be poorly described in the external shell of the H_2 units, we have also performed the calculations with the 6-311G**. Hence we verified that neither the frequency patterns (shifted at most by 4 cm^{-1}) nor the energetics were significantly altered by the change of basis set. This is explained easily by the fact that the H_{2n+1}^{+} clusters are charged species. In addition to HF and $B3(H)$ calculations, a post-Hartree-Fock calculation of a given structure, namely, the Cs one, has also been performed within the CISD method. Since this method is not size consistent, size consistency corrections (SCC's) have been estimated according to Davidson's scheme, as in Ref. 13. Full geometry optimizations have been done, the optimization being stopped when the magnitude of the gradient becomes below 10^{-5} a.u. Vibration frequencies have been evaluated within harmonic approximation from the second derivative analysis.

TABLE I. Typical parameters of the optimized geometries of H_{15}^{+} with $D3h$ symmetry at HF, $B3(H)$/DFT levels of theory. Parameters are defined in Fig. 1.

Method	R (pm)	H (pm)	β (deg.)	P (pm)	γ (deg.)	energy (a.u.)
HF	86.7	222.3	134.9	73.8	90.8	-8.1088
$B3(H)$	87.4	200.4	136.1	74.0	90.0	-8.4117

III. STRUCTURES

A. $D3h$ structure

Figure 1 shows the fully optimized geometry of H_{15}^{+} with $D3h$ symmetry, predicted at the HF level of theory. The optimized structure and the predicted energy are compiled in Table I. In this structure, six H_2 are arranged symmetrically around the H_3^{+} core. Two pairs of the three H_2 molecules are lying above and below of the H_3^{+} plane, respectively. The distance R (86.71 pm) is smaller than those found in the

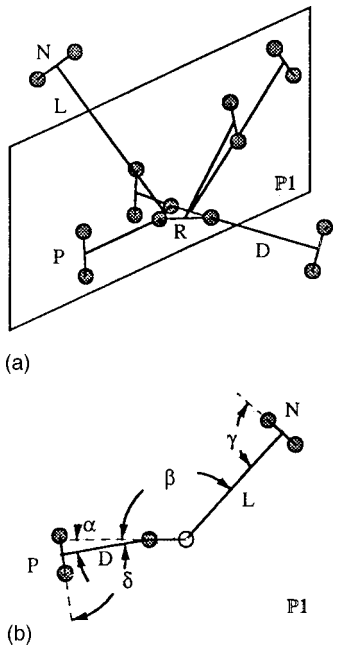

FIG. 2. H_{15}^{+} optimized structure in $C3v$ symmetry.

TABLE II. Typical parameters of the optimized geometries of H_{15}^+ with $C3v$ symmetry at HF, $B3$(H)/DFT levels of theory. Parameters are defined in Fig. 2.

Method	R (pm)	D (pm)	α (deg.)	L (pm)	β (deg.)	P (pm)	N (pm)	γ (deg.)
HF	87.5	179.1	11.5	287.7	132.7	74.1	73.7	88.7
$B3$(H)	88.6	165.8	8.4	283.5	132.3	74.5	73.8	87.1

other structures by approximately 1 pm. The distance H is found to be smaller than the distances $L(H_9^+-H_2)$ but greater than the corresponding distance $D(H_3^+-H_2)$ in the Cs and $C3v$ structures. However, at the HF level, the harmonic vibration analysis exhibits one imaginary frequency, so that the structure could be thought as being a transition state between two $C3v$ structures. Within DFT, the $B3$(H) structure is qualitatively the same with slightly longer bonds in the H_2 units or the H_3^+ core, and a shorter (10%) distance between the H_2 and the H_3^+ core. The vibrational analysis leads to even more imaginary frequencies, since eight imaginary frequencies are found.

The total energy, significantly higher than the $C3v$ and Cs ones, indicates also that this structure is rather a transition state.

B. $C3v$ structure

On the basis of our previous work on H_{11}^+ and H_{13}^+, the $C3v$ structure is obtained by addition of three H_2 molecules to a H_9^+ core (where the H_2 subunits lie nearly perpendicular to the H_3^+ plane). Figure 2 shows the fully optimized geometry for H_{15}^+ with $C3v$ symmetry assignment, predicted at HF level of theory. The optimized parameters structure and the predicted energy are reported in Tables II and IV. Starting from H_9^+, each further H_2 molecule is located in a mediator plane perpendicular to the H_3^+ and going through one apex of the H_3^+ triangle [see plan P1, inset in Fig. 2(a)]. A deformation of the H_9^+ core is observed (angle $\alpha=11.5°$) stronger than for the Cs structure of H_{15}^+ (*vide supra*). The distance L between each added H_2 subunits and the deformed H_9^+ core, about 287 pm, is 1 pm smaller than the corresponding distance in H_{13}^+, 1 pm larger than the corresponding distance in H_{11}^+. The distances between the outer H_2 subunits are on the order 382 pm. This structure is a true minimum in the potential energy surface of H_{15}^+ at this level of theory.

Within the DFT approach, the structure obtained does not differ significantly with the one optimized at HF level described above and is also a true minimum. The main differences lie in shorter H_3^+-H_2 distances, in particular D which concerns the first H_2 shell i.e., the H_9^+ core. Concomitantly, the H_3^+ nucleus is slightly relaxed.

C. Cs structure

Figure 3(a) shows the fully optimized geometry of H_{15}^+ with Cs symmetry, predicted at the three both levels of theory HF, CISD, and DFT/$B3$(H). The optimized structures and the predicted energies are gathered in Tables III and IV. This structure is also a true minimum. The Cs structure is built by addition of three H_2 molecules to a H_9^+ core as the previous structure, but placing two H_2 subunits on one side of the H_9^+ core and the last H_2 on the opposite side [see Fig. 3(a)]. These outer H_2 are found to be off centered with respect to the center of the H_3^+ core. A deformation of the H_9^+ core is observed: H_2 subunits link the H_3^+ plane with an angle $\alpha_2=9.5°$ for both of them and $\alpha_1=6.7°$ for the third one [see Fig. 3(b)]. Moreover, the distances $D1$ and $D2$ are found to differ by 2.36 pm and the central H_3^+ core is not anymore equilateral. The same trend is kept for the CISD and the $B3$(H) calculations.

TABLE III. Typical parameters of the optimized geometries of H_{15}^+ with Cs symmetry at HF, CISD, $B3$(H)/DFT levels of theory. Parameters are defined on Fig. 3.

Method	$R1$ (pm)	$R2$ (pm)	$D1$ (pm)	$\alpha 1$ (deg.)	$D2a$ (pm)	$D2b$ (pm)	$\alpha 2$ (deg.)	$L1$ (pm)
HF	87.5	87.6	179.7	6.7	99.1	190.8	9.5	297.4
CISD	88.6	88.7	168.4	6.8	91.3	183.0	4.5	282.3
$B3$(H)	88.6	88.9	167.2	2.4	89.3	182.4	4.1	277.7

	$\beta 1$ (deg.)	$L2a$ (pm)	$L2b$ (pm)	$\beta 2$ (deg.)	$P1$ (pm)	$\delta 1$ (deg.)	$P2$ (pm)	ε (deg.)
HF	84.3	258.4	184.6	60.4	74.2	90.2	74.2	85.4
CISD	86.9	248.7	174.7	59.8	74.8	90.3	74.8	83.1
$B3$(H)	95.3	242.8	172.0	60.2	74.4	90.4	74.5	81.4

	$\delta 2$ (deg.)	$N1$ (pm)	$\gamma 1$ (deg.)	$N2$ (pm)	η (deg.)	$\gamma 2$ (deg)
HF	97.1	73.7	108.1	73.7	136.8	74.5
CISD	101.0	74.1	103.9	74.1	132.9	65.0
$B3$(H)	95.9	73.8	105.2	73.8	130.5	70.5

TABLE IV. Total energies and dissociation energies (according to $H_{15}^+ \rightarrow H_2 + H_{13}^+$) of the optimized geometries of H_{15}^+ with *Cs* and *C*3*v* symmetries at HF, *B*3(H)/DFT levels of theory. The corresponding zero-point energies (ZPE's) are also given.

Method	Total energies (a.u.)	Dissociation energies (D_e) (kJ mol^{-1})	ZPE (a.u.)
	*C*3*v* symmetry		
HF	-8.1139	1.95	0.1005
*B*3(H)	-8.4185	2.86	0.1012
	Cs symmetry		
HF	-8.1140	2.22	0.1004
CISD[a]	-8.3531[b]	3.14	
*B*3(H)	-8.4186	3.12	0.1014

[a]CISD energy calculated at HF geometry.
[b]Size-consistency correction estimated to -0.02188 a.u.

It is remarkable that all the calculations predict that this structure is more stable than the *C*3*v* one, but the energy difference between the two stable structures amounts only 10^{-4} Hartree (0.03 eV). Typical distances representative of the H_3^+-H_2 interaction (D), the H_9^+-H_2 interaction (L), the H_3^+ core (R), and the H_2 subunits (P and N), have been reported in Fig. 4 for the whole series of clusters H_{2n+3}^+; $n=1$, 6 as obtained in HF and *B*3(H) calculations. When two distances, for example, $P1$ and $P2$ are representative of a distance P, both of them are reported on Fig. 4. We can see that the typical distances of *Cs*-H_{15}^+ follow the same general trend already pointed out with H_{11}^+ and H_{13}^+. D increases with the mass number and reach a nearly constant value ($\sim$177 pm) for n greater than 3. On the other hand, comparing the distances R between the protons in the H_3^+ core one can notice that this core is less deformed in the H_{15}^+ cluster than in the H_{13}^+ cluster. The distances P in the H_2 subunits within the H_9^+ core decrease with n up to a nearly constant value (74.2 pm for H_{15}^+ at HF level). The distances N (73.8 pm) in all other H_2 subunits in H_{15}^+, i.e., the most external are even smaller than the distances P and closer to the 73.6 pm value of free H_2. value. In order to compare efficiently the distance representating the interaction $H_9^+ \cdots H_2$ in H_{11}^+, H_{13}^+, and H_{15}^+, we have reported on Fig. 4 the distance C corresponding to the distance between the outer H_2 subunits and the center of H_3^+. The values obtained for C amounts in HF calculations 290.8, 293.4 and 303.4, 308.3 pm for H_{11}^+, H_{13}^+, and H_{15}^+, respectively. In the *B*3(H) calculation the values are 279.7, 281.3 and 287.9, 288.2 pm, respectively. The value of distance C in H_{15}^+ is 10 pm greater than the value obtained for the other clusters at HF level, the difference is slightly reduced with *B*3(H). We notice that the *Cs* structure of H_{15}^+ includes a pair of H_2 molecules on one side of the H_9^+ core. The distance between the H_2 molecule has been estimated about 349 pm in HF and 341 pm in *B*3(H) calculation in this pair,which is not far from the value (344 pm) of the intramolecular distance of the solid hydrogen.[14]

IV. ENERGETICS

The stability of the clusters can be investigated through the dissociation energies of these clusters according to the reaction $H_3^+(H_2)_{n-1} + H_2 \rightarrow H_3^+(H_2)_n$. As in previous works,[11–13] the dissociation energies De for the abstraction of molecular hydrogen from H_{15}^+ are deduced from the calculation at HF and *B*3(H) levels of theory for the three conformers and sake of comparison at CISD for the *Cs* conformer. The energies required to remove molecular hydrogen from *Cs*-H_{15}^+, *C*3*v*-H_{15}^+, and *D*3*h*-H_{15}^+ are 2.22, 1.95, and -1.16 kJ, respectively, for HF calculations and 3.12, 2.86, and -14.9 kJ for *B*3(H) calculations, to be compared to the experimental value (7.27 ± 0.42) kJ. In Fig. 5 it has been reported together to previous values[11–13] the dissociation energies of $H_3^+(H_2)_n$ $n=1$–6 as calculated within HF

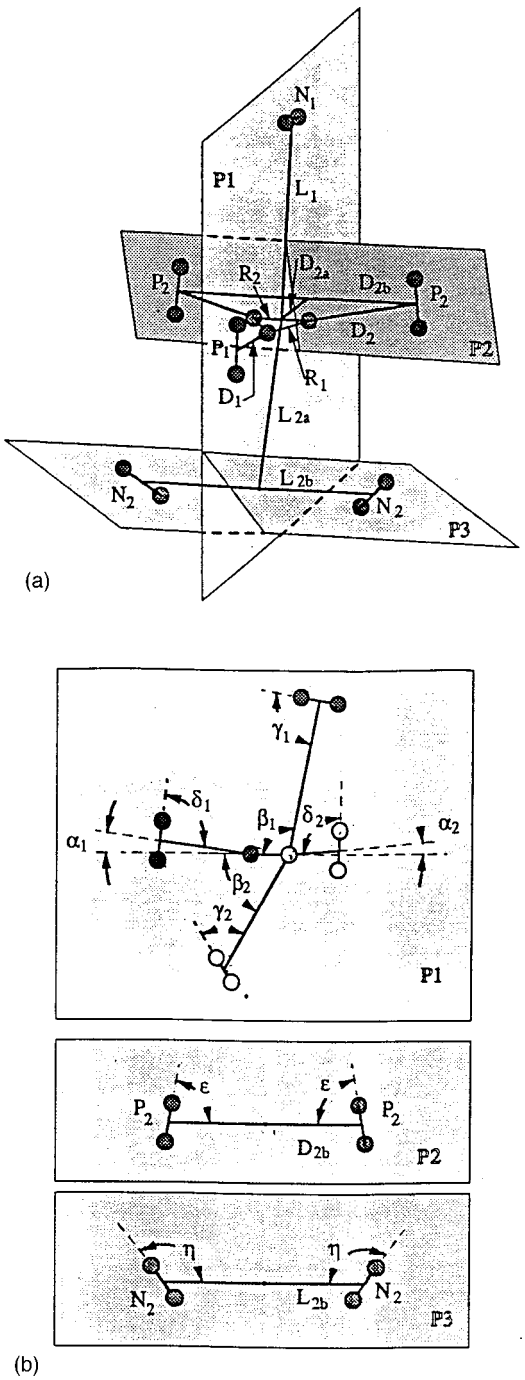

FIG. 3. H_{15}^+ optimized structure in *Cs* symmetry.

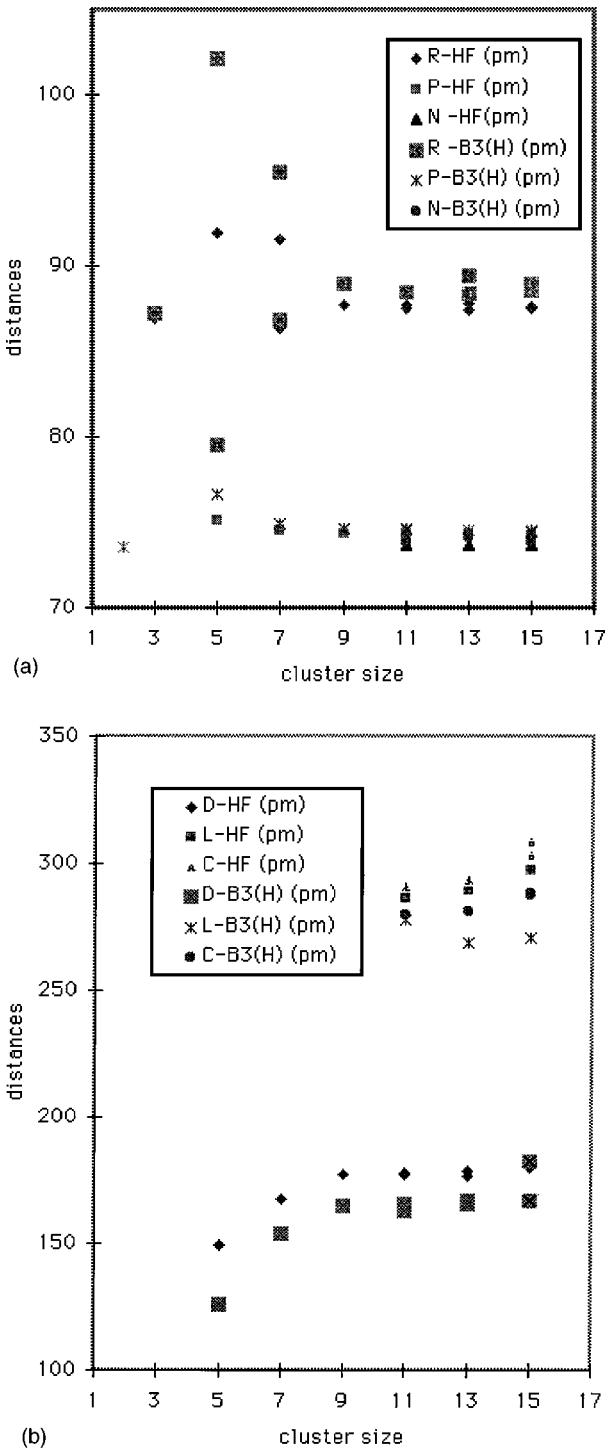

FIG. 4. Typical bond lengths of the optimized geometries of $H_3^+(H_2)_n$ $n=1-6$ at HF and $B3$(H)/DFT levels of theory.

and $B3$(H). The predicted dissociation energies De of H_{15}^+ is found to follow the experimental trend established by Hiraoka and Mori,[4] as for the other cluster sizes. The gap between the stabilities of the H_5^+-H_7^+-H_9^+ group and the H_{11}^+-H_{13}^+ group is kept similar for H_{15}^+. This indicates that H_{15}^+ would not exhibit an enhanced stability (magic number) as proposed in Ref. 3, but not seen in Ref. 17. These energies are definitely lower than those obtained by Stich *et al.* in their simulations,[10] but the reason lies in the generalized gradient approximation they used (namely PW91) which is known to be more bonding for van der Waals systems.[18,19]

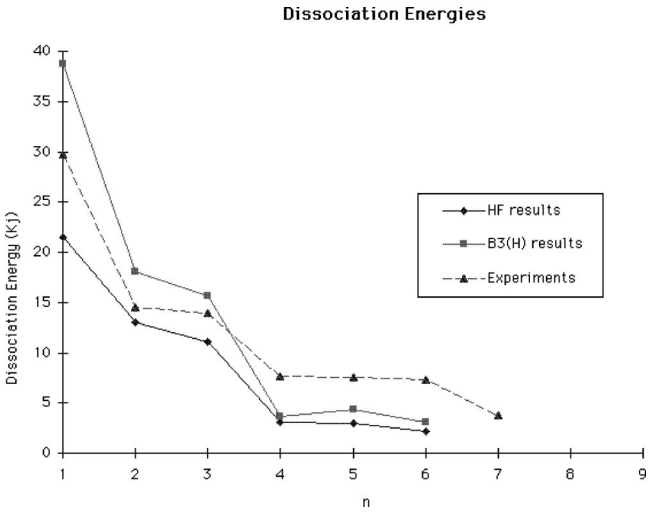

FIG. 5. Theoretical [HF and $B3$(H) level of theory] and experimental (Ref. 4) values of dissociation energies of $H_3^+(H_2)_n$ $n=1-6$.

At the CISD level of theory, a similar poor agreement is obtained for the $De(Cs\text{-}H_{15}^+)$ value, 3.14 kJ, similar to that for H_{11}^+ and H_{13}^+. As previously mentioned, this is traditionaly related to the weakness of the size consistency corrections which are not sufficient. In this kind of system, the size consistency error is rather weak because of the large distance between the H_2 units.

V. VIBRATIONAL FREQUENCIES

Harmonic vibrational frequencies were predicted for the Cs and $C3v$ conformers of H_{15}^+ clusters from HF and $B3$(H) calculations. The results are shown in Tables V and VI. In the Cs-H_{15}^+ case, six frequencies amoung the 39 distinct ones correspond to those arising from the stretching linking the first three H_2 subunits to the H_3^+ core [4503, 4497, 4496, 3427, 2685, 2664 cm^{-1} with HF and 4436, 4426, 4424, 3269, 2477, 2465 cm^{-1} at $B3$(H) level]. Our results exhibit nearly the same theoretical vibrational frequencies as in H_9^+ isolated cluster (4492, 4487 degenerate, 3406, 2656 degenerate cm^{-1} estimated at HF level of theory[12]) and [4424, 4416 degenerate, 3243, 2459, 2447 with $B3$(H) calculation[11]], due to the weak deformation of the H_3^+ core by approaching three H_2 ligands. One of highest mode and the three highest frequencies at 4575, 4574, and 4573 cm^{-1} [4527, 4526, and 4525 cm^{-1} with $B3$(H)] correspond to the three external H_2 vibrations result from the supplementary modes of H_{15}^+ brought by addition of one H_2 to H_{13}^+. Due to the weak H_9^+-H_2 interaction, these vibrational frequencies are smaller than the harmonic frequency predicted for the isolated molecule (4594 cm^{-1} (HF) and 4553 cm^{-1} [$B3$(H)]). These frequencies are also present in H_{11}^+ and H_{13}^+ (4573 cm^{-1}) spectra. Similar features are obtained in the $C3v$-H_{15}^+ case. Taking into account the overestimation of the frequencies inherent to HF method and

TABLE V. Harmonic vibrational frequencies (cm^{-1}) and infrared intensities (in km/mol) with Cs symmetry at the HF and $B3$(H)/DFT levels of theory. No scaling factor has been applied to the frequencies. The increasing order of frequencies has been sligthly altered in order to put identical modes in regard, when possible.

$B3$(H)			HF		
Frequencies	Intensities	Mode	Frequencies	Intensities	Mode
25	3.9	A''	8.2	5.1	A''
43	18.2	A'	36	18.1	A'
88	12.2	A''	62	8.3	A''
90	7.7	A'	76	7.3	A'
107	0.4	A''	78	1.4	A''
120	15.2	A''	88	12.7	A''
140	3.8		100	15.9	A''
141	9.1	A'	109	12.0	A'
143	13.3		118	15.6	A'
152	2.7	A'	120	2.9	A'
162	3.5	A'	125	0.1	A'
163	9.5		129	17.3	A''
177	1.2	A''	137	0.4	A''
185	1.7	A''	151	0.4	A''
197	73.8	A'	155	71.6	A'
201	11.2	A'	160	0.4	A'
206	0.4	A'	160	0	A'
232	19.9	A'	193	58.2	A'
298	20.1	A'	268	35.6	A'
308	16.8	A''	293	26.9	A''
323	13.1	A'	303	22.8	A'
432	448	A'	347	265	A'
459	555	A''	374	420	A''
477	92.8	A'	371	151	A'
640	4.4	A'	597	3.3	A'
649	0.3	A''	599	1.5	A''
728	9.8	A'	691	9.9	A'
822	1.3	A''	700	1.3	A''
858	0.5	A'	764	0.4	A'
881	0.4	A''	771	0.2	A''
2465	931	A''	2664	746	A''
2477	859	A'	2685	701	A'
3269	1.9	A'	3427	1.8	A'
4424	103	A''	4496	85.4	A''
4426	84.2	A'	4497	78.3	A'
4436	26.3	A'	4503	16.3	A'
4525	6.8	A''	4573	4.0	A''
4526	18.1	A'	4574	7.0	A'
4527	1.9	A'	4575	2.5	A'

TABLE VI. Harmonic vibrational frequencies (cm^{-1}) and infrared intensities (in km/mol) with $C3v$ symmetry at the HF and $B3$(H)/DFT levels of theory. No scaling factor has been applied to the frequencies. The increasing order of frequencies has been slightly altered in order to put identical modes in regard, when possible.

$B3$(H)			HF		
Frequencies	Intensities	Mode	Frequencies	Intensities	Mode
50	0	$A2$	42	0	$A2$
55	0.3	E	51	0.6	E
55	0.3	E	51	0.6	E
84	12.8	$A1$	81	15.8	$A1$
116	0.7	E	94	10.0	E
116	0.7	E	94	10.0	E
134	11.2	E	109	8.5	E
134	11.2	E	109	8.5	E
152	0	$A2$	115	0	$A2$
159	11.9	E	132	11.5	E
159	11.9	E	132	11.5	E
170	102	$A1$	132	105	$A1$
166	0	$A2$	148	0	$A2$
176	0.7	E	148	2.2	E
176	0.7	E	148	2.2	E
198	1.0	E	159	0.1	E
198	1.0	E	159	0.1	E
221	23.2	$A1$	182	41.4	$A1$
313	29.1	E	296	68.3	E
313	29.1	E	296	68.3	E
332	1.6	$A1$	311	1.8	$A1$
430	536	E	345	389	E
430	536	E	345	389	E
465	4.0	$A1$	358	4.1	$A1$
644	5.9	E	601	6.4	E
644	5.9	E	601	6.4	E
717	9.4	$A1$	683	10.3	$A1$
802	0	$A2$	679	0.	$A2$
865	3.1	E	763	1.1	E
865	3.1	E	763	1.1	E
2481	868	E	2682	707	E
2481	868	E	2682	707	E
3278	10.8	$A1$	3433	6.1	$A1$
4431	108	E	4500	89.0	E
4431	108	E	4500	89.0	E
4437	2.2	$A1$	4504	2.0	$A1$
4526	8.2	E	4573	5.2	E
4526	8.2	E	4573	5.2	E
4527	10.8	$A1$	4575	5.5	$A1$

$B3$(H) method (because its inclusion of some pure exchange) is usually referred to an anharmonicity correction, although it originates to the stiffness of the HF potential well. Using a scaling factor of 0.89 for HF calculations and 0.91 for $B3$(H) frequencies as explained in Ref. 11, one gets values which are more suitable to be compared to experiment, but the trends discussed here are not altered.

Turning to the symmetric stretching frequency of H_3^+, we found 3427 (3269) and 3433 (3278) cm^{-1} for Cs and $C3v$ symmetry with HF and [$B3$(H)], respectively. These frequencies are correctly found below the equivalent harmonic frequency predicted for the isolated ion [3538 (3500) cm^{-1}]. Likewise, the H_3^+ degenerate bending frequency (2859 cm^{-1}) is reduced by 174 and 195 cm^{-1} in the Cs structure, and by 177 cm^{-1} in the $C3v$ structure. This bending frequency (2799 cm^{-1}) is found reduced by 322 and 334 cm^{-1} and 318 cm^{-1} for Cs and $C3v$ structures with $B3$(H) calculations. The fact that $B3$(H) results

gave the lowest frequencies between our two calculations could be expected since the H_3^+ nucleus is relaxed with $B3(H)$.

Concerning the outer H_2 molecules added in the H_{15}^+, we can also estimate the fundamental frequencies by the scaling procedure reported in Ref. 13 leading to 4139 and 4140 cm^{-1} for the Cs structure and the $C3v$ one, respectively. Concerning the $B3(H)$ results, the scaling factor mentioned above has been used leading to 4118 cm^{-1} for the two structures. These predictions can be connected to the weak shoulders observed near 4080–4100 cm^{-1} in clusters larger than H_9^+ which are certainly due to the absorption by these outer H_2.

As expected, the high frequencies are found higher within HF calculations than in DFT, in agreement with the smaller scaling factor of $B3(H)$ vs HF previously discussed, however, the trend is found opposite for the low frequencies namely in the 50–300 cm^{-1} range. This could be related to larger interactions between H_2 subunits found in DF calculations as evidenced by the shortest H_2-H_2 distances within the cluster.

VI. INFRARED INTENSITIES

In Tables V and VI are also presented in IR intensities obtained in HF and $B3(H)$ calculations for the Cs and $C3v$ H_{15}^+ minima. The fundamental $\nu(A_1)$ and $\nu(A')$(H_2 stretching in the H_9^+ core in both the Cs and $C3v$ structures) observed by Okumura and co-workers,[20] at 4048 cm^{-1} for H_{15}^+ are predicted with moderate intensity, namely, 78.3, 85.4 for the Cs structure and 89 (degenerate) for the $C3v$ one within HF calculation. For the $B3(H)$ calculation the values are 84.2, 103, and 108 (degenerate), respectively. Furthermore, concerning the highest frequencies of H_{15}^+, they are predicted to have low intensities; 4.0, 7.0, 2.5 km/mol in HF calculation and estimated 6.3, 18.2, 1.8 km/mol with $B3(H)$ for the Cs structure, the corresponding values are 5.2 (degenerate) and 5.5 [8.2 (degenerate), 10.8] km/mol for the $C3v$ one [$B3(H)$ values in parenthesis]. Among the normal modes that might be assigned to H-H stretching, the modes at 2664 and 2685 cm^{-1} for the Cs structure and 2682 cm^{-1} doubly degenerate for the $C3v$ one exhibit by far the greatest predicted IR intensities, 746 and 702 km/mol, and 707 km/mol (degenerate), respectively, in HF calculations. These values have been exalted in $B3(H)$ results [931, 859, and 868 (degenerate), respectively] .

VII. CONCLUSIONS

To take into account the apparent high stability of H_{15}^+, as seen in some cluster size distributions and collisional experiments, it has been suggested that the structure of H_{15}^+ should result of a symmmetric addition of six H_2 around an H_3^+ core. We found that this structure is not a minimum. This statement reinforces the conclusion obtained by Diekmann and co-workers.[8] In their paper, they found no planar structure so that they could not confirm the Hiraoka's assumption supposition concerning the relative stability of H_{15}^+. Taking into account our previous results on H_{11}^+ and H_{13}^+, two minima of the potential energy hypersurface of H_{15}^+ are obtained from structures corresponding to nucleation of three H_2 around a H_9^+ core weakly deformed. The Cs structure with two H_2 subunits on one side of the H_3^+, and another one on the opposite is predicted to have the lowest total energy. We notice that this structure includes a pair of H_2 molecules. The distance between the H_2 molecules in this pair, e.g., 349 pm at the CISD level of theory [341 pm with $B3(H)$], is not far from the value (344 pm) of the intramolecular distance in the solid hydrogen.[14]

This work underlines the flatness of the potential energy surface since the $C3v$ structure lies only 0.03 eV higher in energy. One can expect a relatively large fluxionality of the structures, and a great ability to dissociate, in agreement with the low temperature used in experiments and with the Car-Parrinello dynamics performed by Stich *et al.*[9,10]

Indeed the stability of the Cs structure could even be questioned because of the low frequency obtained at HF level (8 cm^{-1}) which is close to the numerical accuracy limit of this kind of computation. However, this frequency is found larger within the DFT $B3(H)$ calculations (25 cm^{-1}). As in previous work[11] we can underline that the $B3(H)$ functional has permitted to obtain structures and energies of H_{15}^+ cluster with a reasonable computational effort and that the structures obtained are qualitatively very similar to HF ones. Moreover, the Cs structure calculated within the CISD method is very close to HF and $B3(H)$ ones, as well as the energetics associated to its dissociation, showing that for such a type of clusters containing rather separated subunits, the lack of size consistency of the CISD method is less dramatic than one could expect.

As already seen for H_{11}^+ and H_{13}^+ species, all the theoretical methods used to study these clusters underestimate the energy dissociation whereas the trends in the description of stability groups is well described. On the other hand, it is worthwhile noting that the HF approach, which totally fails to predict good structures for smallest clusters,[11] leads to results closer to correlated methods as far as the system grows. The H_{15}^+ system is the first one where two H_2 molecules in the shell surrounding the H_9^+ nucleus are located at a distance similar to liquid hydrogen or hydrogen ice. The stability of the H_{2n+3}^+ clusters series can be thought as a result of the interaction of a given number of hydrogen molecules with a seed consisting in a H_9^+ nucleus which itself consists in a H_3^+ nucleus surrounded by three H_2 molecules. The mobility of the second-shell, namely, the molecules around H_9^+ may be rather large since the PES of the $H_3^+(H_{2n})$ clusters with $n > 3$ is flat.

By inspection of the charge distribution, the Mulliken population analysis is highly significant in this kind of system because all atoms hold the same orbital basis set. The analysis obtained from the present calculations have shown that most of the +1 charge is beared by the H_3^+ core (+0.60) and the H_2 of the first shell (H_9^+) (0.11 each), whereas each external H_2 molecules have lost only 0.02 electrons, This is in agreement with the vibrational frequencies spectra of these clusters, for which the most external H_2 molecules exhibit vibrational frequencies close to those of neutral hydrogen.

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