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Structures and Energetics of H_n^+ Clusters ($n = 5-11$)

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Ab initio calculations are performed for the H_n^+ clusters, ($n = 5, 7, 9, 11$) at the coupled-cluster single-double and quasiperturbative triple excitation (CCSD(T)) level of theory. The use of the correlation-consistent basis sequence aug-cc-pVXZ, with X = D, T, Q, facilitated the estimation of their energies in the complete basis set (CBS) limit. Such hydrogen clusters are constituted by a H_3^+ core in which H_2 units are bound. To understand the features of these bindings, shell structures are examined carefully, and bond dissociation energies, enthalpies, and entropies upon cluster formation are computed and compared with available experimental data.

I. Introduction

Protonated hydrogen clusters H_n^+ present the simplest example of molecular clustering and for decades have attracted experimental and theoretical effort to clarify their structures and properties.[1−11] It was found that odd-numbered clusters are much more stable than even-numbered ones.[12] Because of the long-range ion−molecule interaction, they grow easily into higher molecular species, and odd-numbered clusters up to H_{47}^+ have been observed.[13] The structure of these clusters has generally been described as a tightly bound H_3^+ ion core with the H_2 molecules arranged in solvation shells around it, in contrast to the structure of their neutral counterparts.[14] Thus, because of their properties, such clusters have been studied to explore solvation mechanisms in liquids and nucleation phenomena in hydrogen discharges and plasmas in the atmosphere and interstellar medium.

Directly pertinent to the present study, various experiments[1,2,15−17] have been carried out to study the $H_{n-2}^+ + H_2 \rightarrow H_n^+$ clustering reaction. Dissociation enthalpies $-\Delta H^0$ and entropies $-\Delta S^0$ have been measured, and a successive shell formation for H_n^+ clusters with $n = 9$, 15, 19, and 23 is suggested. One of the most detailed experimental studies has been carried out by Okumura et al.[3] using infrared vibrational predissociation spectroscopy. This experiment provided the vibrational frequencies of H_2 and H_3^+ in $H_3^+ \cdot (H_2)_n$ ionic clusters for $n = 1-6$, and the dependence of the shift of these vibrations has been analyzed with the cluster size. Later, Bae[18] extended the photodissociation spectrum of H_5^+, and the four new observed bands have been assigned to overtones of stretching modes of H_3^+ in H_5^+ or combinations of them with the intermolecular stretching mode between H_3^+ and H_2.

A substantial number of theoretical studies on positive hydrogen clusters have been performed. Yamaguchi et al.[19] have performed an extensive CI study on H_5^+ in order to characterize the potential surface of the cluster. Spirko and Kraemer[20] performed MR-CI calculations, and by fitting their data to an analytical many-body expansion, they have calculated the vibrational levels of the H_5^+ cluster. Prosmiti et al.[21] performed QCISD(T)/cc-pVQZ calculations, and they proposed an analytical DIMPT1 form to describe the H_5^+ potential surface. Nagashima et al.[6] were the first to deal with larger clusters (up to $n = 16$) by using a classical Monte Carlo approach based on a sum of site−site interactions fitted to ab initio MP4 data to describe the intermolecular potential. Later, Pang[8] used quantum Monte Carlo simulation to study the electronic structures of ionic hydrogen clusters with $n = 9$. Stich et al.[9] proposed a combined molecular dynamics and density functional theory (DFT) approaches to study H_n^+ up to $n = 27$, and Ignacio and Yamabe[10] studied odd hydrogen clusters up to $n = 21$ by using the G2(MP2) approach. Recently, larger H_n^+ clusters with $n = 13-27$ have been studied[11,22] using the MP4/6-311G(2p) level of theory, and DFT calculations employing the B3(H) functional have been performed[23,24] for H_{15}^+ and H_{21}^+.

In this article, we present results of high-level ab initio calculations on the structure, energy, and thermochemistry of the first-shell protonated hydrogen clusters up to H_{11}^+. CCSD(T,FC)/CBS energies are estimated by extrapolating the results of aug-cc-pVXZ, X = D, T, Q, basis set calculations performed at the optimal CCSD(T) configurations for each cluster. The purpose of this study is to refine/correct previous estimates of structure, vibrational frequencies, binding energies, enthalpies, and entropies of these systems and compare them with available experimental data.[17]

II. Computational Details

All ab initio calculations were performed using the Gaussian 98 package.[25] Geometries of the H_n^+ stationary points were optimized at CCSD(T) level of correlation treatment using aug-cc-pV(T/Q)Z, Dunning's triple/quadruple-ζ correlation-consistent basis set. Vibrational frequency calculations were carried out at the same level of theory. They were used to characterize the stationary points and to compute zero-point vibrational and corresponding corrections to the binding energies of H_n^+ clusters. Molecular energies for the H_n^+ clusters with $n = 3-11$ were calculated at the complete basis set limit. The CBS energies were computed by performing CCSD(T) calculations using aug-cc-pVXZ, X = D, T, Q, basis sets at the optimal CCSD(T)/aug-cc-pV(T/Q)Z structure for each H_n^+ cluster. For

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TABLE 1: Bond Lengths (Å) of Optimized Structures for H_2 and H_n^+ ($n = 3-11$) Obtained in the Present Work

cluster	$R_1/R_2/R_3$	$D_1/D_2/D_3$	$P_1/P_2/P_3$	L	N
H_2			0.74186		
$H_3^+(D_{3h})$	0.87367				
$H_5^+(C_{2v})$	0.97738/0.81275	1.29289	0.76641		
	0.974/0.820^b	1.314^b	0.779^b		
	0.9951/0.8101^c	1.2546^c	0.7685^c		
	0.994/0.806^d	1.2508^d	0.765^d		
	1.13/1.13^e	1.06^e	0.81^e		
$H_5^+(D_{2d})$	1.12502/0.78487^f	1.05436^f	0.78487^f		
$H_7^+(C_{2v})$	0.94115/0.87211	1.57382	0.75496		
	0.9472/0.8723^c	1.5519^c	0.7544^c		
	0.947/0.870^d	1.551^d	0.751^d		
	1.03/0.89^e	1.45^e	0.78^e		
$H_9^+(D_{3h})$	0.89034	1.66154	0.75367		
	0.8901^c	1.658^c	0.7502^c		
	0.889^d	1.657^d	0.748^d		
	0.92^e	1.62^e	0.77^e		
$H_{11}^+(C_s)$	0.89040/0.88665	1.67352/1.69325	0.75316	2.59369	0.74662
	0.8904/0.8874^c	1.6556/1.6728^c	0.7496/0.7494^c	2.7358^c	0.7424^c
	0.891/0.887^d	1.649/1.669^d	0.748^d	2.630^d	0.740^d
	0.92/0.92^e	1.61/1.59^e	0.76^e	2.72^e	0.77^e

[a] See the text and Figure 1 for notation. [b] Reference 8. [c] Reference 7. [d] Reference 10. [e] Reference 9. [f] Reference 21.

$E_{\rm CBS}$, the following mixed exponential/Gaussian functional form[26] is used:

$$E(x) = E_{\rm CBS} + Be^{(-(x-1))} + Ce^{(-(x-1)^2)} \qquad (1)$$

$x = 2$ for aug-cc-pVDZ, 3 for aug-cc-pVTZ, and 4 for aug-cc-pVQZ basis sets. The above form has been found to yield better agreement with experimental data than other functional forms in several studies.[27−30] The binding energies are given by

$$D_{\rm e}^{\infty} = E_{\rm CBS}(H_n^+) - [E_{\rm CBS}(H_{n-2}^+) + E_{\rm CBS}(H_2)] + E_{\rm BSSE} \qquad (2)$$

where $E_{\rm BSSE}$ is the correction for the basis set superposition error (BSSE), computed using the counterpoise method of Boys and Bernardi.[31] The enthalpy variation for the $H_n^+ \rightarrow H_{n-2}^+ + H_2$ dissociation is calculated by

$$\Delta H = [H_{(H_{n-2}^+)} + H_{H_2}] - H_{H_n^+} \qquad \text{or}$$

$$\Delta H = -D_{\rm e}^{\infty} + \Delta(\mathrm{ZPE}) + \Delta(\epsilon(T)) \qquad (3)$$

where H represents the enthalpies for H_2 and each H_n^+ cluster calculated as

$$H^{298.15} = E_{\rm CBS} + \mathrm{ZPE} + \epsilon(T) \qquad (4)$$

ZPE represents the zero-point vibrational energy corrections, and $\epsilon(T)$, the thermal corrections for H_2 and H_n^+ clusters. Zero-point vibrational energies as well as thermal corrections are calculated at the CCSD(T)/aug-cc-pVQZ level for H_2 and H_n^+ ($n = 3-7$) and at the CCSD(T)/aug-cc-pVTZ level for $n = 9$ and 11. Entropy variations are also computed by $\Delta S = [S_{(H_{n-2}^+)} + S_{H_2}] - S_{H_n^+}$, where S stands for the entropies calculated for H_2 and each H_n^+ ($n = 3-11$) cluster.

III. Results

The geometries of H_n^+ clusters are characterized using Cartesian coordinates, and for their presentation here we use only the following coordinates (Figure 1): R_1, R_2, and R_3 are the H−H bond lengths in the H_3^+ monomer, P_i and N denote the H−H distances of the first and second shells of H_2 monomers, respectively, D_i represents the intermolecular distances of one (the nearest) H atom of H_3^+ to the center of mass of the first shell of H_2, and L is the distance of the midpoint of the closer R_i bond of H_3^+ to the center of mass of the second shell of the H_2 molecule.

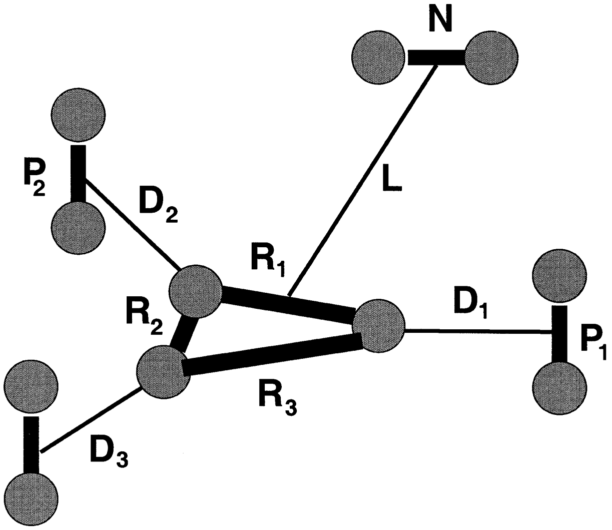

Figure 1. Schematic representation of the coordinates for H_n^+ clusters.

The results of CCSD(T)/aug-cc-pV(T/Q)Z calculations for the optimized structures of H_n^+ clusters are presented in Table 1 and depicted in Figure 2. The total CCSD(T) energies of the above optimal configurations using aug-cc-pVQZ basis sets as well as their CBS limits (eq 1) are listed in Table 2. For comparison purposes, we summarize in Tables 1 and 2 the best results for each of the H_n^+ clusters available in the literature. The present ab initio calculations reproduce the stationary points for all H_n^+ clusters in accordance with earlier theoretical studies,[7−11,21] although with much lower CBS total electronic energies and some changes in the bond lengths (Tables 1 and 2). The H_2 and H_3^+ molecules are presented here as test cases for evaluating the method and the basis sets used.

For the H_5^+ cluster, the 1-C_{2v} structure has the lowest energy, and the 2-D_{2d} structure, which corresponds to the transition state for the intermolecular proton transfer, is found to be higher in energy by only 0.20 kcal/mol in the CBS limit.

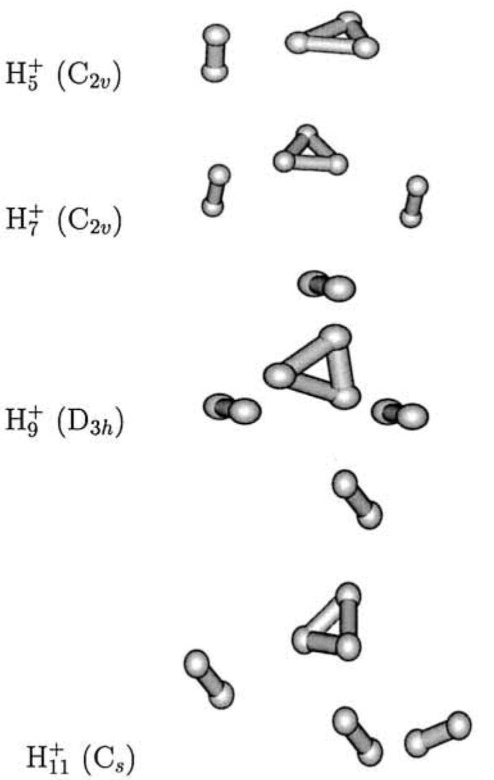

Figure 2. Optimized CCSD(T)/aug-cc-pVQZ structures for the H_n^+ clusters with $n = 5-11$.

TABLE 2: Total CCSD(T) Energies and Their CBS Limits (hartrees) for H_2 and the Indicated H_n^+ Clusters with $n = 3-11$

cluster	CCSD(T)/aug-cc-pVQZ	CCSD(T)/CBS	literature
H_2	−1.173867	−1.17441	−1.174475[32]
$H_3^+(D_{3h})$	−1.343162	−1.34378	−1.343836[33]
$H_5^+(C_{2v})$	−2.530697	−2.53198	−2.531600[8]
$H_5^+(D_{2d})$	−2.530399	−2.53166	−2.530217[21]
$H_7^+(C_{2v})$	−3.712637	−3.71453	−3.713300[8]
$H_9^+(D_{3h})$	−4.893535	−4.89600	−4.894200[8]
$H_{11}^+(C_s)$	−6.071088	−6.07408	−6.051830[11]

Because of this small energy difference, the results for both configurations are presented. The predicted CBS energy for the $H_5^+(C_{2v})$ configuration is 0.24 kcal/mol lower than the one obtained by the diffusion quantum Monte Carlo (DQMC) method,[8] and the D intermolecular distance and the P bond length are shorter by 0.02 and 0.01 Å, respectively. For H_7^+ and H_9^+, the energy differences between the DQMC result and the present one are 0.77 and 1.13 kcal/mol, respectively, whereas for H_{11}^+ a difference of 13.96 kcal/mol is obtained in the total electronic energy in comparison with CCSD(T)/6-311G(1p) calculations.[11] Furthermore, changes are found in the intermolecular distances D and L and the bond lengths P and N of the first- and second-shell H_2 molecules for H_n^+ with $n = 5-11$. In particular, by comparing with the TZP/CISD and G2,MP2/6-311G** results[7,10] the D, P, and N distances are slightly elongated in our calculations for all $n = 5-11$ clusters, and the R bond lengths of the H_3^+ core are shorter, as is the L distance (by 0.142 and 0.036 Å) for H_{11}^+.

To characterize the stability of the above structures and to compute thermodynamic properties, we performed vibrational frequency analysis at the optimal cluster structures. In Table 3, we present the results of the ab initio calculations on the vibrational frequencies of H_2 and the H_n^+ conformers with $n = 3-11$. We should note that for H_{11}^+ the CCSD(T)/aug-cc-pVTZ vibrational analysis predicts that the present structure corresponds to a first-order saddle point. Several trials to locate the structure of a minimum for nearby geometries of H_{11}^+ have not succeeded, indicating an extremely flat potential in the region of the H_{11}^+ stationary point. In Table 3, low frequencies refer to angular deformations of the outer shell of H_2 molecules, and the high-frequency bands correspond to the stretching vibrations of H_2 and H_3^+ units. These frequencies are close to the frequencies of the free H_2 and H_3^+ and are getting closer as the cluster size increases or for clusters whose H_3^+ core is less deformed. Comparing with previous theoretical calculations[5,7] shows that the present frequencies are smaller than the CI/DZ+P[5] and CISD/TZP[7] frequencies for H_5^+ and H_7^+, respectively. Also, reduced values are obtained for the high frequencies of H_9^+ and H_{11}^+ clusters, and their low frequencies are increased compared with the CISD/TZP and SCF/TZP[7] results.

TABLE 3: Harmonic Frequencies (cm^{-1}) for H_2 and H_n^+ ($n = 3-11$) Clusters Calculated at the CCSD(T) Level of Theory

H_2	$H_3^+(D_{3h})$	$H_5^+(C_{2v}/D_{2d})$	$H_7^+(C_{2v})$	$H_9^+(D_{3h})$	$H_{11}^+(C_s)$
					−45 A″
					5 A′
					83 A″
					107 A″
					117 A′
				110 E′	119 A″
				112 E′	128 A″
				186 A_2″	131 A′
				210 A_1″	163 A′
				219 E″	276 A′
			93 A_2	219 E″	340 A′
			126 B_1	454 A_1′	446 A′
			167 A_1	474 E′	469 A″
			404 B_2	475 E′	474 A′
			563 A_1	657 E″	615 A″
		206 A_2/−531 B_2	574 B_1	657 E″	615 A′
		495 A_1/224 B_1	695 A_2	732 A_2″	713 A′
		812 B_2/962 E	733 B_2	738 A_2′	758 A″
		866 B_1/962 E	798 B_1	827 E″	792 A′
		1170 B_1/1411 A_1	904 A_2	827 E″	794 A″
	2772 E′	1838 A_1/1593 E	2291 A_1	2462 E′	2491 A′
	2773 E′	2131 B_2/1593 E	2522 B_2	2462 E′	2500 A″
	3437 A_1′	3668 A_1/3892 B_2	3285 A_1	3198 A_1′	3241 A′
					4275 A′
				4240 E′	4275 A″
			4234 B_2	4240 E′	4280 A′
4403		4115 A_1/3965 A_1	4236 A_1	4246 A_1′	4375 A′

In Table 4, the calculated frequencies of the H_2 and H_3^+ stretching modes for H_2 and for various H_n^+ clusters are listed and compared with the experimental data.[3,18] The ab initio frequencies are given in the harmonic approximation, and scaling procedures have been proposed in the literature[19,34] for obtaining theoretical fundamental/anharmonic vibrational frequencies in better agreement with the ones observed experimentally. We should note that scaling factors have been determined utilizing sets of individual vibrations of different molecules, thus their use globally is questionable, particularly in systems with high anharmonicity. However, a scaling factor of 0.9538 is used here, as is recommended,[34] and the values given in parentheses in Table 4 refer to the above scaled ab initio frequencies.

Using the scaling procedure, we get better agreement with the experimental data. In particular, for ω_1 and ω_2 in H_5^+, the predicted values lie 15 and 33 cm^{-1} above and below the assigned fundamentals of Okumura et al.,[3] respectively, and for ω_8, we compute a scaled value of 472 cm^{-1} that is higher than the approximate experimental value of 320 cm^{-1} (ref 3) by 152

TABLE 4: Experimental and Theoretical Harmonic and Scaled[a] Frequencies (cm^{-1}) of the H_2 and H_3^+ Stretching Modes for H_2 and H_n^+ ($n = 3-11$) Clusters

cluster	symmetry	experiment	this work/CCSD(T)
H_2		4401,[b] (4161)[35]	4403(4200)
$H_3^+(D_{3h})$	A_1	3175[36]	3437(3279)
	E	2521[36]	2772(2644)
$H_5^+(C_{2v})$	A_1	4400,[c] 3910[3]	4115(3925)
	A_1	4060,[c] 3532[3]	3668(3499)
	$(\omega_1 + \omega_8)$	4230[3,18]	4610(4397)
	$(\omega_2 + \omega_8)$	3870[3]	4163(3971)
$H_5^+(D_{2d})$	A_1		3965(3782)
	B_2		3892(3712)
	$(\omega_1 + \omega_8)$		4189(3996)
	$(\omega_2 + \omega_8)$		4116(3926)
$H_7^+(C_{2v})$	A_1	3980[3]	4236(4040)
	B_2		4234(4038)
$H_9^+(D_{3h})$	A_1'	4020[3]	4246(4050)
	E'		4240(4044)
$H_{11}^+(C_s)$	A'	4028[3]	4375(4173)
	A'		4280(4082)
	A''		4275(4077)
	A'		4275(4077)

[a] In parentheses. [b] Harmonic frequency for H_2.[35] [c] Estimated harmonic frequencies for ω_1 and ω_2 in H_5^+.[18]

cm^{-1}. For ω_3 and ω_4, our scaled estimates of 2033 and 1753 cm^{-1} are much lower, by 488 and 768 cm^{-1}, respectively, than the corresponding degenerate asymmetric stretching frequency of the H_3^+ molecule at 2521 cm^{-1}.[36] However, the difference is smaller compared with previous full CI/DZP calculations.[19] The latter frequencies are closer to the H_3^+ values for the rest of the H_n^+ clusters and in particular for H_9^+ and H_{11}^+. This indicates that H_3^+ forms an independent core as the size of the cluster increases.

The calculated frequencies of the H_2 moieties in the H_n^+ clusters are found to be red shifted from the vibrational H_2 frequency with shifts between (27−120) and 275 cm^{-1}. For H_5^+, we obtained the larger red-shift value (275 cm^{-1}), and as the cluster size increases, the frequency is shifted to values closer to the frequency of the H_2 monomer. Thus, for H_9^+, the frequency shift is 150 cm^{-1}, and for H_{11}^+, the frequency shifts for the outer and inner H_2 molecules are 27 and about 120 cm^{-1}, respectively. For H_{11}^+, the frequencies of the inner H_2 are shifted by 30 cm^{-1} from the corresponding frequency for H_9^+. Lee and co-workers[3] have observed red shifts from the monomer H_2 frequency between 130 and 250 cm^{-1}; that for H_5^+ is smaller than the ones predicted by the CCSD(T) calculations, whereas those for the remaining clusters are higher. However, given the high anharmonicity in some vibrational modes of the H_n^+ systems, we consider these results to be in accordance with experimental[3] and previous theoretical predictions[5,7,10] of the nature of the binding that supports a shell structure for the H_n^+ clusters.

Furthermore, the dissociation energies of $H_n{}^+$ to $H_{n-2}^+ + H_2$ with $n = 5-11$ are reported in Table 5. Our predictions for D_e^∞ and D_0^∞ are based on the CBS energies (eqs 1 and 2). The predicted energies required to remove a molecule of hydrogen from H_5^+, H_7^+, H_9^+, and H_{11}^+ are 8.65, 5.12, 4.43, and 2.30 kcal/mol, respectively. By including the zero-point vibrational energies, the D_0^∞ values become 5.91, 2.37, 1.87, and 1.68 kcal/mol, respectively. We should note that the zero-point vibrational energies are not scaled in the above calculation.

In Table 5, we also present the values of enthalpy and entropy variations $-\Delta H$ and $-\Delta S$, respectively, obtained from CCSD(T) calculations for the $H_{n-2}^+ + H_2 \rightarrow H_n^+$ clustering reactions. The $-\Delta H$ values are based on the E_{CBS} values for each cluster (eqs 3 and 4). Enthalpy values are given for 298.15 K; they are corrected at $T = 153$ K for comparison with previous calculations[10,11] and are included in braces. By comparing the above values with the results of previous theoretical studies,[10,11,22] we found that H_5^+ is more stable and that small differences from the scaled G2(MP2) results are obtained for H_7^+, H_9^+, and H_{11}^+. The enthalpy values decrease rapidly from H_5^+ to H_7^+, but for H_9^+, a variation of only 0.25 kcal/mol is obtained at 298.15 K, indicating the completion of the first solvation shell. Several experimental measurements[1,2,15−17] are available for the equilibria of the $H_{n-2}^+ + H_2 \rightarrow H_n^+$ clustering reactions over the temperature range of 25−330 K. Generally, the $-\Delta H$ value increases with the temperature, thus for an easier comparison with the experimental data, enthalpy variations are also computed at an average temperature $\bar{T}$ for each cluster. These average values for the temperature are estimated from the experimental van't Hoff plots[16,17] at 284, 149.5, 127, and 83 K for the H_n^+ clusters with $n = 5$, 7, 9, and 11, respectively. For these temperatures, enthalpy values of 7.36, 2.81, 2.51, and 1.39 kcal/mol are predicted for each H_n^+ cluster. The comparison of

TABLE 5: Electronic Energy Difference (D_e^∞) and Zero-Point Energy Inclusive Electronic Energy Differences (D_0^∞) along with the Corresponding Reaction Enthalpies (kcal/mol) and Reaction Entropies (cal/mol K) for the Successive Dissociation Reactions $H_n^+ \rightarrow H_{n-2}^+ + H_2$ with $n = 5-11$

cluster	D_e^∞	D_0^∞	ΔH^{298} $\{\Delta H^{153}\}$	$\Delta H^{\bar{T}}/\bar{T}$	ΔH_{exptl}	ΔS_{theor}	ΔS_{exptl}
$H_5^+(C_{2v})$	8.6474	5.9068	7.39{7.10}	7.36/284	7.01 ± 0.1[17]	19.31	18.1 ± 2[17]
	7.87[22]		{6.20}[10]	5.89/190[22]	6.9 ± 0.3[16]	16.6[11]	
	7.84[11]		{6.91}[11]	5.26/30[22]	6.6 ± 0.35		
					9.6[2]		
					9.7[1]		
$H_7^+(C_{2v})$	5.1204	2.3655	3.11{2.82}	2.81/149.5	3.3 ± 0.2[16]	17.71	17.4 ± 1[16]
	4.93[22]		{3.00}[10]	3.58/190[22]	3.1 ± 0.1[15]	17.1[11]	
	4.90[11]		{4.24}[11]	2.93/30[22]	4.1[2]		
					1.8[1]		
$H_9^+(D_{3h})$	4.4302	1.8734	2.85{2.56}	2.51/127	3.2 ± 0.2[16]	23.50	18.5±1[16]
	4.21[11]		{3.38}[10]	3.29/190[22]	3.8[2]	18.3[11]	
	4.18[11]		{3.69}[11]	2.63/30[22]			
$H_{11}^+(C_s)$	2.3030	1.6809	1.82{1.53}	1.39/83	1.72 ± 0.1[16]	16.45	17.9±1[16]
	1.56[22]		{1.47}[10]	1.06/190[22]	2.4[2]	14.1[11]	
	1.53[11]		{1.11}[11]	0.31/30[22]			

[a] Available experimental values are also listed.

these values with the experimental ones[16,17] shows deviations of 0.25, 0.29, 0.49, and 0.23 kcal/mol, respectively, which for the larger clusters should be considered high, although chemical accurancy (±1 kcal/mol) is achieved. Finally, entropy variations $-\Delta S$ for H_n^+ are compared with the corresponding experimental values,[17] where agreement within the experimental error bars is found, with an exception for H_9^+, where a larger decrease is predicted in forming this cluster.

IV. Conclusions

Ab initio calculations for the H_n^+ clusters ($n = 5-11$) at the CCSD(T) level of theory are presented. Optimal structures and harmonic vibrational frequencies are calculated, and their total energies are computed in the complete basis set limit using a sequence of three correlation-consistent aug-cc-pVXZ basis sets with X = D, T, Q.

Employing more extended basis sets with a CBS extrapolation of the CCSD(T) energies, we found the smallest members of the series, H_5^+ and H_7^+, to be more stable than in previous theoretical predictions,[5,7,10] and for all of the clusters studied, changes in their optimal configurations are obtained. In particular, tighter structures are predicted for the H_3^+ core, whereas the intermolecular distances between the H_3^+ and H_2 molecules are increased in the first-shell clusters and decreased in the second-shell cluster of H_{11}^+. The high sensitivity to the level of theory indicates the flatness of the potential surface in the neighborhood of the optimal structure of the clusters. In the same vein, differences in the vibrational frequencies and thus in the zero-point energies are also found, with reduced values for H_5^+ and H_7^+ clusters as well as for the high frequencies of the larger clusters, and most of the low intermolecular frequencies for H_9^+ and H_{11}^+ are increased. In turn, concerning the H_2 stretching frequencies of the H_2 molecules in the clusters, the predicted values compare fairly well with the experimental results by Lee and co-workers,[3] supporting a shell structure for the H_n^+ clusters.

Enthalpy and entropy variations for the clustering reaction $H_{n-2}^+ + H_2 \rightarrow H_n^+$ are also computed and compared with experimental estimates.[16,17] The enthalpy variations are calculated for an averaged temperature for each cluster formation according to the experimental van't Hoff plots. Generally, good quantitative agreement is found, with the larger discrepancies observed for the H_9^+ cluster, where a larger decrease in the entropy variation of formation is estimated by the theoretical calculations.

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