Molecular clusters of hydrogen, deuterium and tritium: especially cationic species $H_3^+(H_2)_m$: m=2, 5 and 14

I.A. Howard[a], F.E. Leys[a], N.H. March[a,b], C. Van Alsenoy[c], J.A. Alonso[d] and A. Rubio[d]

[a]Department of Physics, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium
[b]Oxford University, Oxford, England
[c]Department of Chemistry, University of Antwerp,
Universiteitsplein 1, B-2610, Antwerp, Belgium
[d]Donostia International Physics Center (DIPC), San
Sebastian 20018, Spain

ABSTRACT

Two recent experimental studies by Zweiback *et al.* [*Phys. Rev. Lett.* **84**, 2634 (2000)] and by Gobet *et al.* [*Phys. Rev. Lett.* **89**, 183403 (2002)] have motivated us to study the ground-state geometry and the consequent electronic structure of the singly-charged cationic hydrogen cluster $H_3^+(H_2)_m$ for m=2,5 and 14, using at first the Hartree-Fock approximation. For the H_7^+ cluster the fully optimized ground-state geometry yields an isosceles triangle H_3, with charge $\sim 0.85|e|$, and sides 0.852 and 0.884 Å, flanked by two H_2 molecules lying parallel to each other, with bond lengths of 0.740 Å. In contrast, for the H_{13}^+ cluster, the central 'building block' is equilateral H_3 with bond length 0.861 Å, and with charge $\sim 0.815|e|$. This configuration of H_3 is flanked by three almost-parallel H_2 molecules with bond length 0.739 Å. MP2 refinements of geometry, charge distribution and normal mode vibrational frequencies of the cationic tritium cluster T_7^+ and the corresponding deuterium cluster D_{13}^+ are also reported. Finally, Hartree-Fock and MP2 results are recorded for H_{31}^+.

Keywords: Hydrogen, Cluster, Cationic

1. INTRODUCTION

Two very recent experimental studies of Gobet *et al.*[1] and Zweiback *et al.*[2] on hydrogen cluster ions of the form $H_3^+(H_2)_m$ with $m \leq 14$ have given motivation for the present theoretical investigation. However, in the present report, our focus will be, first of all, on the fully optimized ground-state geometry, and the consequent electronic structure and charge distribution in three specific cluster ions of the above type, with m=2,5 and 14, using the Hartree-Fock approximation.

The outline of the paper is then as follows. In section 2 we report on the small cluster ions H_7^+ and H_{13}^+. Our findings closely 'mimic' the structural formula $H_3^+(H_2)_m$ already written, in that the central unit in each cluster ion at the HF level of approximation is indeed a H_3 triangle carrying most ($\sim$ 80%) of the unit positive charge of the cluster ion. Attention is also given in section 2 to the vibrational frequencies of these clusters H_7^+ and H_{13}^+. Section 3 considers changes due to inclusion of corrections to Hartree-Fock from second-order Möller-Plesset perturbation theory. H_{31}^+ is studied in section 4.

2. SMALL CLUSTER IONS H_7^+ AND H_{13}^+ : GROUND-STATE GEOMETRIES AS PREDICTED BY THE HARTREE-FOCK APPROXIMATION

Geometry optimizations and subsequent determinations of normal mode vibrational frequencies were carried out using Gaussian 98[3] with the 6-31G** basis.

Further author information: (Send correspondence to I.A.H.)
I.A.H.: E-mail: howard@ruca.ua.ac.be

2.1. Equilibrium geometry of H_7^+

The fully optimized ground-state geometry as predicted by the HF method is shown in Figure 1. The central unit is seen to be a triangular configuration H_3 which is isosceles, with sides of length 0.852 and 0.884 Å. This configuration is found to carry some 85% of the total resultant positive charge of unity of this cluster ion. The central unit is flanked by two almost-parallel H_2 molecules, having bond length 0.740 Å, which are nearly perpendicular to the triangle, and whose centres of mass lie in the plane of the triangle. For the two corners of the triangle flanked by dimers, the distance from the corner of the triangle to either atom of the nearest dimer is 1.846 Å.

2.2. Geometry and charges for cationic cluster H_{13}^+

In contrast, when we turn to consider H_{13}^+, the central unit with three protons has now essentially the form of an equilateral triangle with sides of length 0.861 Å, in the HF approximation. As shown in Figure 2, this triangle is flanked by three almost-parallel H_2 molecules with bond lengths of 0.739 Å, again oriented nearly perpendicularly to the plane of the triangle, with their centres of mass in the plane of the triangle. The remaining two dimers sit above the plane of the triangle. There is a little less of the resultant charge of this cationic cluster on the triangle ($\sim$ 81.5%) than for H_7^+, but the difference is quite small. To test the intrinsic stability of these HF structures for H_7^+ and H_{13}^+, we turn immediately to discuss the vibrational frequencies of the normal modes.

2.3. Normal mode vibrational frequencies for H_7^+ and H_{13}^+ clusters at Hartree-Fock level

The frequencies recorded in Table 1 for the 15 normal modes are actually given for the tritium cation T_7^+. However, to the numerical accuracy of the HF results, one simply scales according to $1/\sqrt{m}$, with m the isotopic mass, to obtain the corresponding frequencies for H_7^+ and D_7^+. The most important qualitative conclusion is that all the frequencies are real, testifying to the intrinsic stability of the cluster geometry at the HF level. Table 2 records similar results for the deuterium cation D_{13}^+. Before discussing the vibrational data further, it is important to consider the modifications to (a) ground-state equilibrium geometry, (b) charge distribution and (c) vibrational frequencies brought about by refining these HF studies by second-order Möller-Plesset perturbation theory (MP2).

Table 1. Normal mode vibrational frequencies of cationic cluster $T_3^+(T_2)_2$

Mode	T_7^{+1} (cm^{-1}) HF	T_7^{+1} (cm^{-1}) MP2	Mode	T_7^{+1} (cm^{-1}) HF	T_7^{+1} (cm^{-1}) MP2
1	38.0	44.2	9	354.5	436.2
2	49.5	45.9	10	438.1	525.0
3	75.3	98.8	11	1577.0	1455.0
4	187.3	150.8	12	1635.0	1568.0
5	204.9	236.8	13	2069.0	2030.0
6	262.6	321.2	14	2599	2572.0
7	320.4	354.6	15	2600.0	2573.0
8	343.4	392.6			

3. CHANGES DUE TO INCLUSION OF MP2 TERMS IN PROPERTIES OF CLUSTERS H_7^+ AND H_{13}^+

3.1. Equilibrium geometry and charges

Figure 3 shows the changes in the optimized cluster geometry brought about by adding MP2 corrections to the HF results shown in Fig. 1 for H_7^+. The overall structure remains largely intact. But while the 'intramolecular' geometry of H_3 and H_2 molecular ions is hardly changed at a quantitative level, the 'intermolecular' geometry is more sensitive. Thus a 'near-neighbour' H-H distance for such interactions of 1.85 Å in our HF calculations is significantly reduced to 1.70 Å with a corresponding (small) reduction of the charge on the central triangular unit. Figure 4 shows the 'MP2-refined' structure of H_{13}^+ and similar conclusions obtain: the distance from a corner of the triangle to either atom of the nearest dimer is reduced from 1.922 Å at HF level to 1.796 Å at MP2 level. We turn, to complete this section, to a tabulation of the refinements of the vibrational frequencies for the two cation clusters considered in Tables 1 and 2 at the HF level. Changes usually are around a maximum of 50 cm^{-1} from the HF results. The MP2 refinements are shown alongside the HF modes in these two Tables.

Table 2. Normal mode vibrational frequencies of cationic deuterium cluster $D_3^+(D_2)_5$

Mode	D_{13}^{+1} (cm^{-1}) HF	D_{13}^{+1} (cm^{-1}) MP2	Mode	D_{13}^{+1} (cm^{-1}) HF	D_{13}^{+1} (cm^{-1}) MP2
1	10.5	12.0	18	224.4	234.5
2	38.9	38.9	19	236.2	242.9
3	49.4	53.4	20	357.1	386.6
4	61.8	60.0	21	359.8	388.2
5	64.3	62.2	22	392.2	412.6
6	70.2	70.9	23	433.3	532.9
7	71.5	75.7	24	468.5	546.6
8	72.8	80.6	25	469.6	549.5
9	83.8	83.3	26	1975.	1885.
10	91.7	86.0	27	1990.	1904.
11	94.4	91.9	28	2520.	2463.
12	99.8	108.8	29	3195.	3168.
13	103.9	111.4	30	3197.	3170.
14	111.2	130.8	31	3199.	3173.
15	148.8	131.9	32	3256.	3237.
16	162.0	145.4	33	3257.0	3238.0
17	203.4	223.2			

It is relevant here to note that trial runs on cluster ions with m=3 and 4 suggest to us rather strongly that electron correlation may play a more substantial role in determining their equilibrium structure than for the cases m=2 and 5, whose optimized geometries using MP2 are reported in this section.

Having discussed these two smallest cluster ions with $m = 2$ and 5 at some length, we next consider the largest cluster ion used in the experiments of Gobet *et al.*,[1] namely $H_3^+(H_2)_m$ with m=14.

4. GEOMETRY, CHARGING AND VIBRATIONAL MODES OF H_{31}^+ CLUSTER AT HARTREE-FOCK AND MP2 LEVELS

The optimized geometry of H_{31}^+ at MP2 level is depicted in Figure 5. The basic configuration seen in the previous clusters persists, with a central (isosceles) triangle of sides 0.864 and 0.869 Å, and three nearly-parallel dimers of bond length 0.741 Å, oriented in a similar fashion to those in the smaller clusters considered. The remaining dimers have a slightly reduced bond length of about 0.735 Å, and form a 'cage' around this central unit. Table 3 records the 87 vibrational frequencies at HF and MP2 levels for the cluster $H_3^+(H_2)_{14}$. Note that modes 71 through 73 are clearly associated with the internal vibrations of the central triangle, while modes 74 through 87 are essentially H_2 internal vibrations. The effect of MP2 refinement here is to reduce somewhat these higher-lying frequencies.

Table 3. Vibrational frequencies of cationic species $H_3^+(H_2)_{14}$. For comparison, the frequencies for isolated H_3^{+1} are 2944.0, 2948.0, 3666.0 cm^{-1} (HF) 2905.0, 2909.0, 3663.0 cm^{-1} (MP2) and for neutral H_2 4638.0 cm^{-1} (HF) and 4611.0 cm^{-1} (MP2). (The table continues on the next page)

Mode	H_{31}^+ (cm^{-1}) HF	H_{31}^+ (cm^{-1}) MP2	Mode	H_{31}^+ (cm^{-1}) HF	H_{31}^+ (cm^{-1}) MP2
1	10.6	7.9	45	142.5	136.5
2	11.1	8.7	46	142.9	137.7
3	13.3	14.9	47	145.7	138.8
4	17.0	16.7	48	148.5	140.1
5	21.1	20.2	49	150.0	141.1
6	21.7	21.9	50	151.8	152.8
7	22.6	24.6	51	152.7	157.4
8	24.8	26.8	52	155.7	162.7
9	27.8	29.0	53	161.2	166.6
10	31.5	31.2	54	169.0	169.3
11	34.0	34.5	55	179.5	175.0
12	36.1	35.3	56	194.7	179.3
13	38.4	42.8	57	198.5	188.1
14	40.7	45.7	58	199.7	189.8
15	42.6	45.9	59	204.3	195.3
16	44.8	51.6	60	213.2	199.9
17	45.8	52.5	61	220.1	218.6
18	47.9	53.6	62	280.8	313.9
19	49.7	54.3	63	316.9	324.6
20	52.9	56.0	64	332.0	347.1
21	53.6	59.5	65	503.3	544.3
22	57.8	63.3	66	512.7	564.5
23	59.8	66.0	67	558.5	605.8
24	64.4	69.9	68	607.3	743.8
25	64.9	76.2	69	645.1	749.3
26	67.3	77.5	70	658.9	780.0
27	68.4	77.9	71	2798.	2667.
28	71.9	79.0	72	2808.	2674.
29	75.0	81.4	73	3562.	3477.
30	77.2	83.3	74	4521.	4480.
31	81.8	89.6	75	4527.	4490.
32	86.1	90.7	76	4530.	4496.
33	87.7	98.2	77	4611.	4583.
34	93.7	101.5	78	4611.	4583.
35	95.6	104.4	79	4611.	4583.
36	100.5	106.9	80	4612.	4583.

Mode	H_{31}^+ (cm^{-1}) HF	H_{31}^+ (cm^{-1}) MP2	Mode	H_{31}^+ (cm^{-1}) HF	H_{31}^+ (cm^{-1}) MP2
37	109.2	109.1	81	4612.	4584.
38	111.7	110.9	82	4613.	4584.
39	113.2	113.1	83	4624.	4595.
40	116.4	115.7	84	4624.	4596.
41	124.5	117.8	85	4626.	4599.
42	130.4	120.0	86	4626.	4599.
43	132.0	128.0	87	4627.	4600.
44	137.6	135.2			

5. SUMMARY AND DISCUSSION

The cluster ions $H_3^+(H_2)_m$, $m \leq 14$ used in the experimental work of Gobet *et al.*[1] have here been studied by Hartree-Fock theory. For the clusters with $m = 2$, 5 and 14, second-order Möller-Plesset perturbation theory has been used to refine the HF results. The overall geometries remain similar, but the effect on 'intermolecular' H-H bond lengths is to significantly shorten and thereby to strengthen bonding in some of these. The vibrational frequencies of the H cluster ions considered typically change by less than 50 cm^{-1} for the higher frequencies, all the frequencies being real at each level of approximation. The 'structural' formula $H_3^+(H_2)_m$ for m=2 and 5 is fairly realistic in that about 80 % of the resultant ionic charge $|e|$ is found to reside on the central H_3 triangle in both clusters at each of the levels of approximation used.

We have thought it of interest to also investigate the case $m = 0$ for HF and MP2 levels; in each case the geometry is that of an equilateral triangle, with at the HF level a bond length of 0.855 Å, which at MP2 level shifts negligibly to 0.857 Å. In this context we also looked at the binding energy of H_7^+ and H_{31}^+ relative to the cationic trimer plus neutral dimers; at MP2 level, the binding energy of H_7^+ is then found to be 0.344 eV, while that of H_{31}^+ is 0.679 eV.

In conclusion, we think the theory of such clusters of H, D and T will be of increasing interest as experimental studies build up. The experimental work of Zweiback *et al.*[2] on nuclear fusion driven by Coulomb explosion of large deuterium clusters presents a major challenge for theory. By driving explosions in such D clusters by means of a 35 fs laser pulse, these workers have accelerated ions to sufficiently large kinetic energies that DD nuclear fusion is produced. The fusion yield from exploding D clusters is found to vary strongly with cluster size, and obviously theoretical work on the acceleration of deuterons via Coulomb explosion forces is an area of great interest for cluster theorists in the future.

As this paper was approaching completion, we became aware of the spectroscopic experiments of Momose *et al.*[4] on $\gamma-$ray ionized parahydrogen ($p-H_2$) crystals. The authors infer this ionization to involve three stages (i) to (iii), of which (iii) is highly relevant to the present investigation. Stage (i) is ionization of H_2. Stage (ii) is an ion-neutral reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

while stage (iii) they term stabilization. The H_3^+ cation attracts neighbouring H_2 in their picture. The present study, though of course now for a free-space molecular cluster ion rather than in a $p-H_2$ crystalline environment, makes quantitative their 'stage (iii)' proposal above. It is worth noting, in conclusion, their observed transition frequencies near 4150 cm^{-1}, but it would be speculation presently to infer that these connect with our free-space normal mode frequencies, especially as they consider the transition near 4150 cm^{-1} to be associated with the macroscopic electric field.

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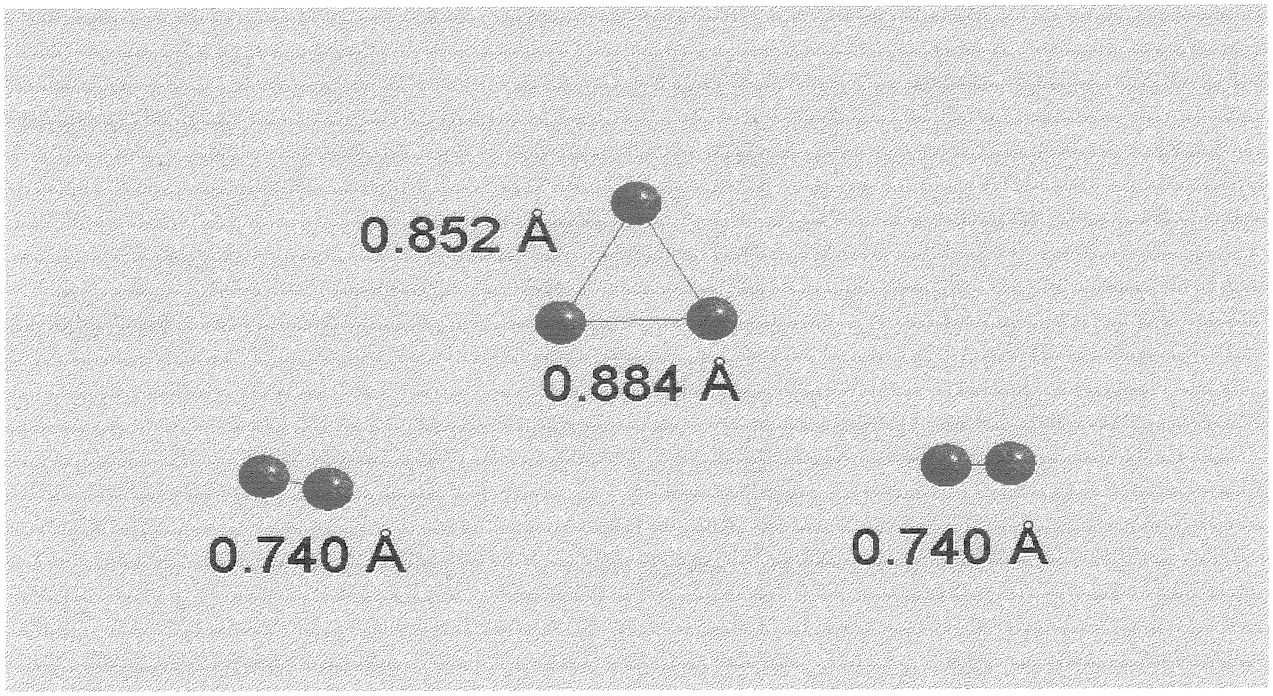

Figure 1. Geometry of H_7^+ at HF level.

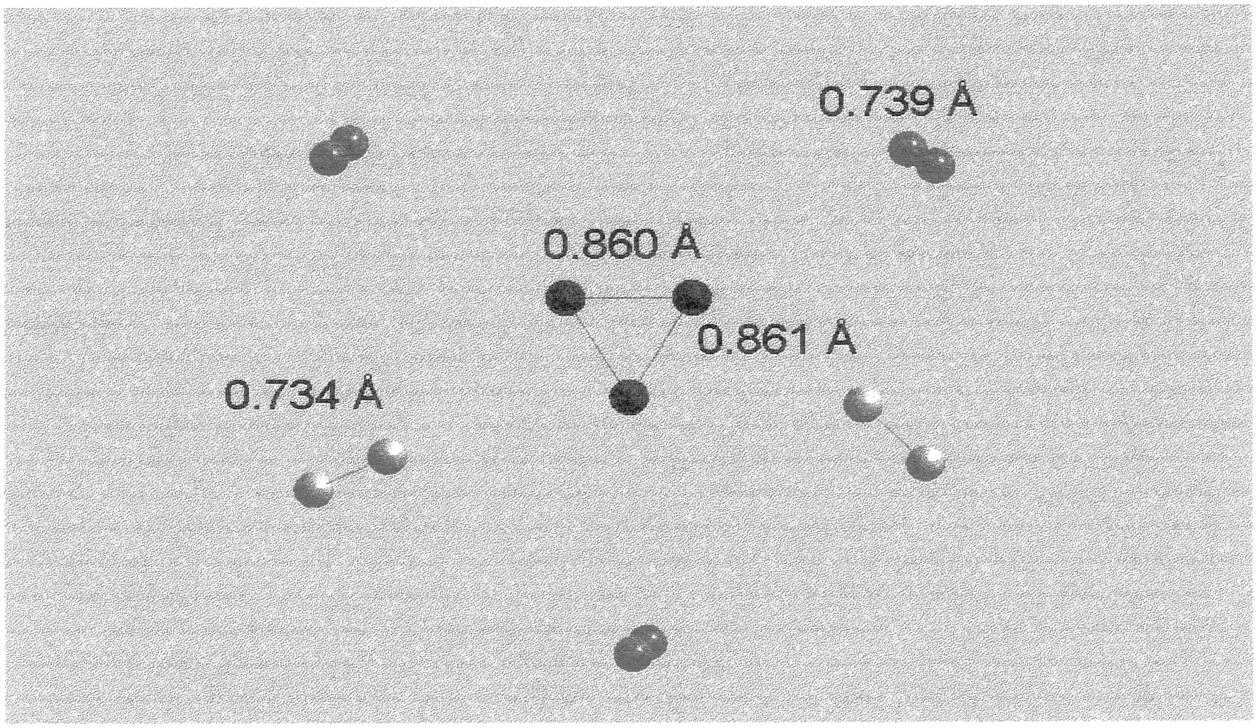

Figure 2. Geometry of H_{13}^+ at HF level.

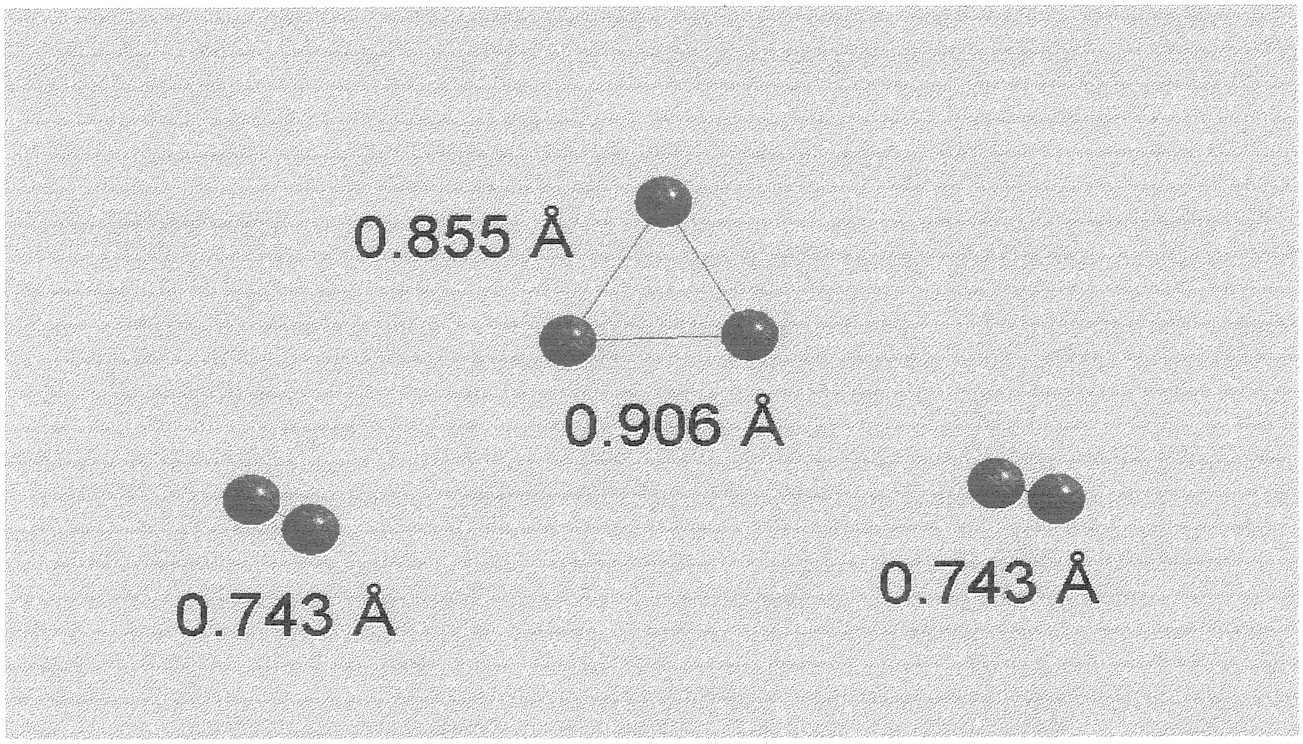

Figure 3. Geometry of H_7^+ at MP2 level.

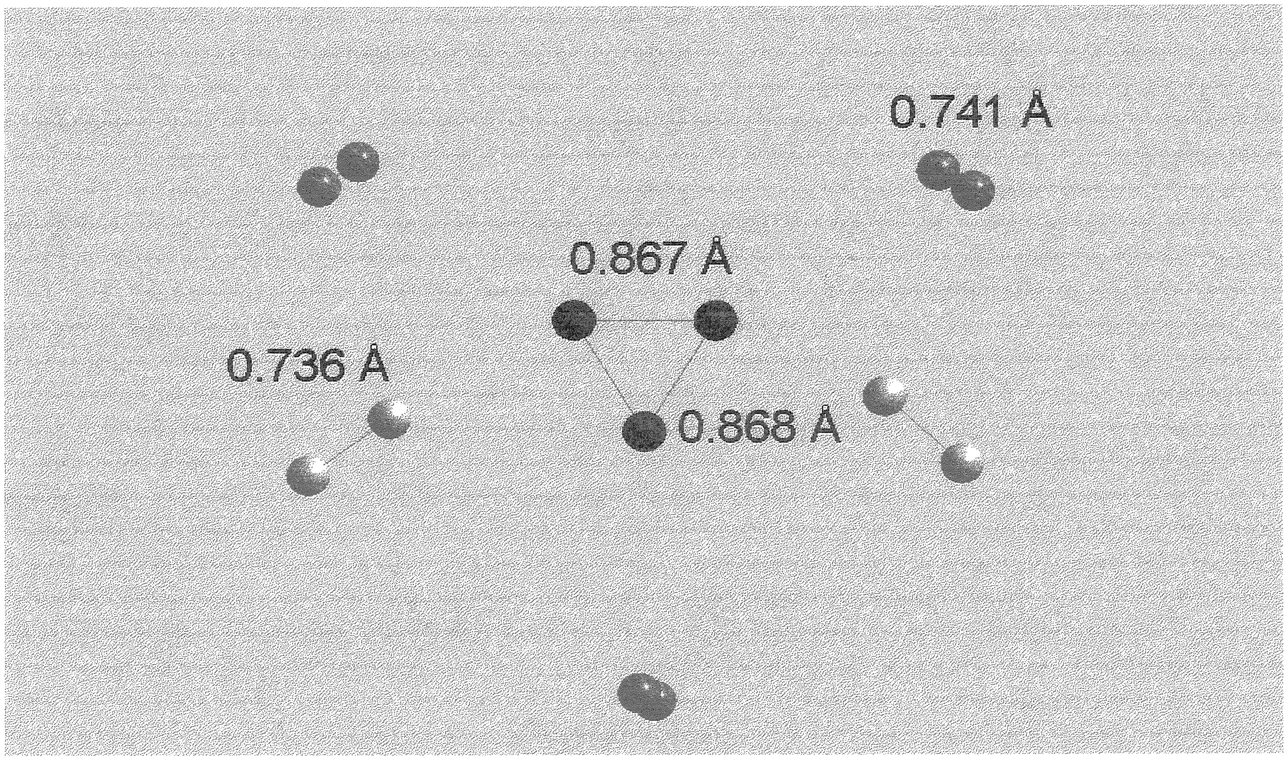

Figure 4. Geometry of H_{13}^+ at MP2 level

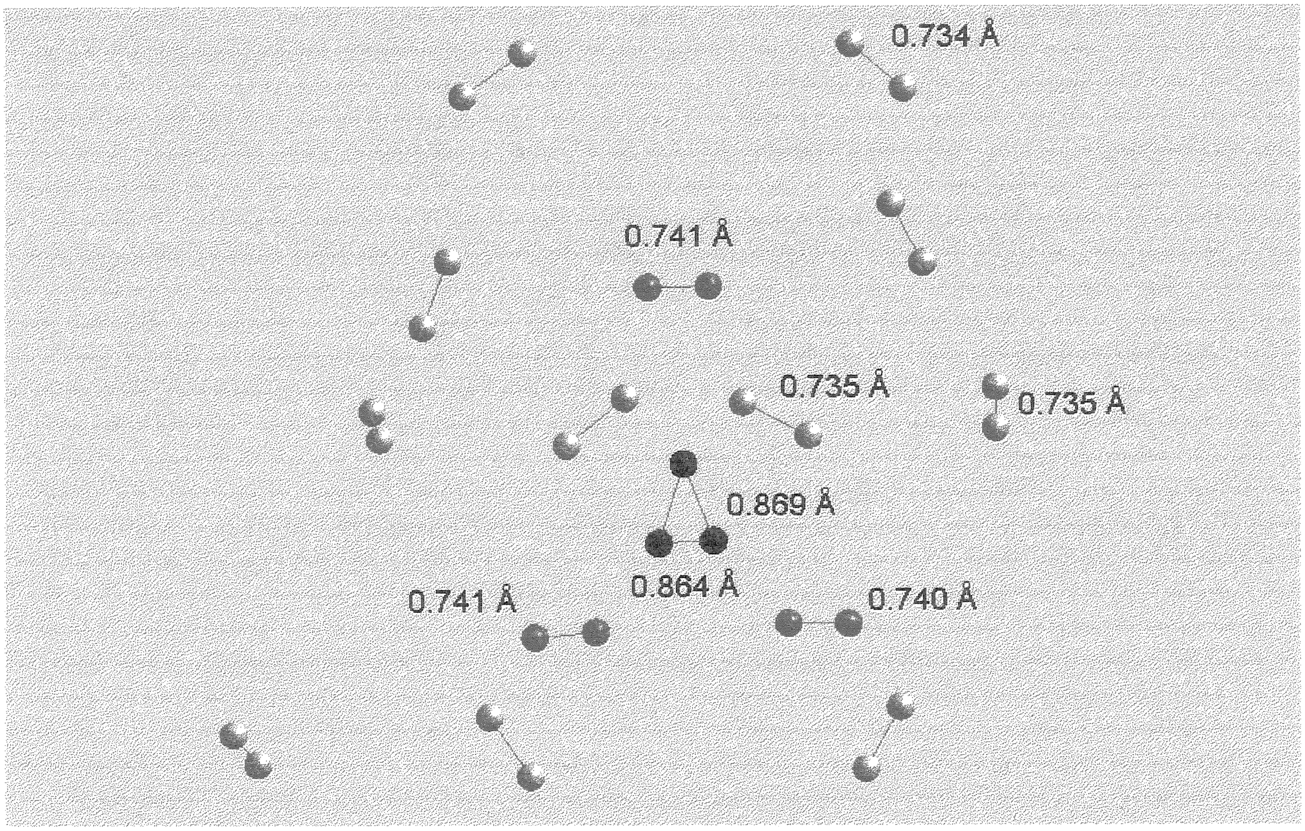

Figure 5. Geometry of H_{31}^+ at MP2 level