Structures and Stabilities of $\text{H}_3^+ (\text{H}_2)_n$ Clusters (n=1-11)

B. Diekmann, P. Borrmann, E.R. Hilf

Department of Physics, Carl v. Ossietzky University Oldenburg, D-26111 Oldenburg, Germany

Abstract

Geometries and energies for $\text{H}_3^+ (\text{H}_2)_n$ clusters (n = 0, ..., 11) have been calculated using standard "ab initio" methods. Up to clusters with n = 6, four different Pople basis sets (DZ, TZ, TZP) have been used in the calculations. For larger cluster sizes, the calculations have been carried out with one basis set (DZ) using the HF/CISD method. We discuss here only the nice counterplay of polarisation effects between the central $\text{H}_3^+$ ion and the adsorbed $\text{H}_2$ molecules, which naturally governs both the geometric structure and the energy of the clusters.

Please regard: This article is also available in the WWW under the URL:

http://www.physik.uni-oldenburg.de/Docs/documents/UOL-THEO3-94-5/cont.html

Typeset using REVTeX
I. INTRODUCTION

H$_3^+$ molecules have been first experimentally verified in 1912 [1], Dawson and Tickner have identified H$_3^+(H_2)$ clusters by mass spectrometry in 1962 [3]. In a recent work of Kirchner and Bowers on this topic [3] [4], the dynamics of metastable H$_3^+(H_2)$ fragmentations are studied. Another experimental work of Hiraoka and Mori [5] deals with the stability of H$_3^+(H_2)_n$ clusters.

Many theoretical studies of small H$_3^+(H_2)_n$ clusters ( n $\leq$ 3 ) have been published in the last years. Yamaguchi, Gaw, Remington and Schaefer [6] have made an intensive study of H$_3^+(H_2)$ with the Pople Double Zeta plus Polarization Basis (DZP), H$_3^+(H_2)_2$, H$_3^+(H_2)_3$, H$_3^+(H_2)_4$ and H$_3^+(H_2)_5$ have been calculated with the Triple Zeta plus Polarization Basis (TZP) by Farizon, Farizon-Mazuy, Castro Faria and Chermette [7], [8] and [9]. To our knowledge, this ab initio calculation is the first calculation for H$_3^+(H_2)_n$ clusters for n larger than 5. We will study here clusters up to $n = 11$ and compare the lighter ones the results of Farizon et al. The results will be discussed in terms of geometrical isomerization.

II. NUMERICAL PROCEDURE

The geometric optimization of the hydrogen clusters was implemented here by the BERNY-algorithm [10]. In the optimization no restrictions in bond-lengths and bond-angles have been adopted. The geometric construction of the clusters is done sequentially, starting with an optimized H$_3^+$ structure with a randomly placed H$_2$ molecule added at a distance of about 3.5 Å from the H$_3^+$. In a first run the position of the new H$_2$ has been optimized, in a subsequent calculation all geometric variables have been optimized. The optimizations of the larger clusters are performed analogously with each new H$_2$ molecule placed randomly at a distance of about 3.5 Å from the last added H$_2$ molecule.

For the electronic configuration we selected the CISD/DZ and the CISD/TZP model for two sets of calculations. With regard to the electron-correlation effects in H$_2$ and H$_3^+$, CI
calculations should be used [11].

For our intention to make predictions for larger clusters, we compare a model on a relatively low theoretical level but suited to be used for larger clusters, with a more sophisticated ansatz, both applied to small clusters. After comparing these results it should be possible to extrapolate properties of larger clusters using the simpler ansatz.

For our extensive numerical calculations we adopted the GAUSSIAN 90 and GAUSSAIN 92 code [12] on a S400/4 supercomputer [13], which has a peak performance of 5 GFlops. Calculations of such relatively large systems with such large basis sets were only possible by use of an extra 1 GB ram-memory besides the main memory of up to 1 GB. The calculations took all in all about 200 cpu hours.

The procedure described above has been tested by application to \( \text{H}_3^+ \) and \( \text{H}_3^+(\text{H}_2) \) clusters, which have been investigated thoroughly before.

The results of the calculations of the \( \text{H}_3^+(\text{H}_2) \) cluster are in good agreement with the results of FARIZON et al. [7] and with other theoretical work.

III. RESULTS AND DISCUSSION

The theoretical calculations, which include correlation effects of the electrons, reduce the energies of the systems. Regarding the electrostatic properties of the \( \text{H}_2 \) molecules, it is necessary to use polarization functions in these methods in geometric calculations.

Fig. 1 and Fig. 2 display the electron density in \( \text{H}_3^+(\text{H}_2) \) calculated with the TZP basis from different views. Apparently the \( \text{H}_2 \) is most tightly bound when closest to one of the hydrogens of \( \text{H}_3^+ \) pushing the negative charges to the other two hydrogens in the \( \text{H}_3^+ \).

The more subtle effect of the orientation of the \( \text{H}_2 \) is predicted by the TZP calculations to be perpendicular to the \( \text{H}_3^+ \)-plane. Thus the electrons of \( \text{H}_2 \) are most distant from the electrons within the \( \text{H}_3^+ \).

With the less sophisticated basis set DZ (two instead of six basis functions per electron) geometric optimization yields a quite different result. The polarization is less pronounced
and incomplete, yielding a completely planar structure. The electron charges in the H$_3^+$ are almost equidistributed over the three protons. Interestingly the electron density between the H$_2$ and the H$_3^+$ comes out too low, resulting in a reduction of the binding energy of as much as 0.05 a.u. .

Understanding what happens in this smallest cluster makes it easy to understand the larger structures, too.

The H$_3^+(H_2)_2$ and H$_3^+(H_2)_3$ clusters are built by the same structure principle, while the charge distribution is more amusing (the corresponding geometry structures are shown in figure 4 and figure 5). A nice example of charge frustration occurs in the H$_3^+$, which means that the charges are being repelled from all H$_2$ symmetrically and assemble in the middle of the H$_3^+$ triangle.

A first geometric and energetic shell is filled with these three molecules as is also indicated by the differences in the energies, which are give in figure 7.

For a study of the relative stability of the clusters we define a value which reflects that the H$_3^+(H_2)_n$ clusters are a composition of H$_2$ and H$_3^+$ molecules

$$l := \frac{E_{H_3^+}}{E_{H_3^+} + \frac{2-3}{2}E_{H_2}},$$  

as a measure of the relative stability of the clusters. The relative stability reduces while the cluster size increases.

Magic numbers using these defined $l$-values may be inferred for $n = 3, 5, 9$ using DZ. The relative stability of H$_3^+(H_2)_5$ has been predicted by Hirao and Yamabe [14] in a geometric consideration. In the experimental work of Hiraoka [5] the H$_3^+(H_2)_6$ seems to be more stable than its neighbours. Hiraoka related this to a total planar geometry of H$_3^+(H_2)_6$ . We could not confirm this and found no planar structure.

The magic numbers of $n = 3, 5, 9$, see figure 7, demonstrate the packing of the H$_2$ , where three of them form the innermost shell, while the next shell consists of four H$_2$ .

In the calculations the model of the positive H$_3^+$ center of the cluster with neutral H$_2$ molecules has been verified.
A property of the geometry of the clusters are the interatomic distances of the H$_2$ molecules. This effect depends directly on the distance from the positive H$_3^+$ center of the cluster perturbated by the other H$_2$ as shown in figure 6. The interatomic distances of the H$_2$ molecules decrease with increasing distance of those molecules from the H$_3^+$ center. This is another nice polarization effect which can be understood in the following manner. The positive central charge attracts the electrons of the H$_2$ reducing the screening of the protons of the H$_2$ which in turn enlarges the repulsion between them.

We have calculated H$_3^+$(H$_2$)$_n$ clusters up to $n = 11$, the largest H$_3^+$(H$_2$)$_n$ cluster calculated so far. We observe two glooming obstacles: The optimization reveals more and more geometric isomers (second minima in the energy) with more and more shallow barriers. In addition the complexity of the basis set necessary for a reliable calculation should increase exponentially which is prevented by the computational resources. Finally the kinetic energies of the atoms contribute to the total energy of the clusters substantially and are not taken into account in the codes used here.
REFERENCES

[1] J.J. Thomson. *Phil. Mag.*, 24, 209, 1912.

[2] P.H. Dawson and A.W. Tickner. *J. Chem. Phys.*, 37, 672, 1962.

[3] N.J. Kirchner, J.R. Gilbert, and M.T. Bowers. *Chem. Phys. Lett.*, 106, 1984.

[4] N.J. Kirchner and M.T. Bowers. *J. Chem. Phys.*, 86, 3, 1987.

[5] K. Hiraoka. A determination of the stabilities of $h_3^+(h_2)_n$ with $n = 1−9$ from measurements of the gas-phase ion equilibria $h_3^+(h_2)_{n-1} + h_2 = h_3^+(h_2)_n$. *J. Chem. Phys.*, 87 (7), 1987.

[6] Y. Yamaguchi, Jeffrey F. Gaw, Richard B. Remington, and Henry F. Schaefer III. The $h_5^+$ potential energy hypersurface: Characterisation of ten distinct energetically low-lying stationary points. *J. Chem. Phys.*, 86, 9, 1987.

[7] M. Farizon, B. Farizon-Mazuy, N.V. de Castro Faria, and H. Chermette. *Chem. Phys. Letters*, 177, 4, 1991.

[8] M. Farizon, B. Farizon-Mazuy, N.V. de Castro Faria, M.J. Gaillard, and H. Chermette. *Phys. Rev. A*, 45, 179, 1991.

[9] M. Farizon, B. Farizon-Mazuy, N.V. de Castro Faria, and H. Chermette. *Chem. Phys. Letters*, 96, 2, 1992.

[10] H.B. Schlegel. *J. Comput. Chem.*, 3 (2), 214, 1970.

[11] B. Diekmann. Geometrien and Stabilitätseigenschaften von $H_3^+(H_2)_n$ clustern, 1993. Diploma Thesis, Univ.Oldenburg, Germany, Pub.No.: UO-93-7.

[12] Gaussian, Inc., 4415 Fifth Avenue, Pittsburgh, PA 15213.

[13] Fujitsu Vektorrechner S400 des RRZN (Regionalen Rechenzentrum Niedersachsen) Schloßwenderstr., D-30159 Hannover.

[14] K. Hirao and S. Yamabe. *Chem. Phys. Letters*, 80, 237, 1983.
FIGURES

FIG. 1. Contour plot of the electron density of $\text{H}_3^+(\text{H}_2)$ with TZP basis taken in the plane of $\text{H}_3^+$.  

FIG. 2. Contour plot of the electron density of $\text{H}_3^+(\text{H}_2)$ with TZP basis taken perpendicular to the plane of $\text{H}_3^+$.  

FIG. 3. Contour plot of the electron density of $\text{H}_3^+(\text{H}_2)$ with DZ basis taken perpendicular to the plane of $\text{H}_3^+$.  

FIG. 4. Three dimensional view of the $\text{H}_3^+(\text{H}_2)_3$ structure.  

FIG. 5. Three dimensional view of the $\text{H}_3^+(\text{H}_2)_3$ structure.  

FIG. 6. $\text{H}_3^+(\text{H}_2)_n$ Geometric properties: interatomic distances of $\text{H}_2$ as a function of the cluster size.  

FIG. 7. $\text{H}_3^+(\text{H}_2)_n$ Stabilities: l-value of $\text{H}_3^+(\text{H}_2)_n$ clusters as a function of the cluster size.  

FIG. 8. Three dimensional view of the $\text{H}_3^+(\text{H}_2)_5$ structure.  

FIG. 9. Three dimensional view of the $\text{H}_3^+(\text{H}_2)_7$ structure.
TABLE I. Energies (a.u.) of $\text{H}_3^+ (\text{H}_2)_n$ cluster calculations

|        | HF/TZP  | RCISD/DZ | RCISD/TZP |
|--------|---------|----------|-----------|
| $\text{H}_3^+ (\text{H}_2)$ | -2.46232 | -2.51659 |
| $\text{H}_3^+ (\text{H}_2)_2$ | -3.61718 | -3.68837 |
| $\text{H}_3^+ (\text{H}_2)_3$ | -4.77087 | -4.85857 |
| $\text{H}_3^+ (\text{H}_2)_4$ | -5.84204 | -5.91698 |
| $\text{H}_3^+ (\text{H}_2)_5$ | -7.06959 | -7.18842 |
| $\text{H}_3^+ (\text{H}_2)_6$ | -8.10608 | -8.21822 |
| $\text{H}_3^+ (\text{H}_2)_7$ | -9.36654 | |
| $\text{H}_3^+ (\text{H}_2)_8$ | -10.37204 | -10.51389 |
| $\text{H}_3^+ (\text{H}_2)_9$ | -11.66103 | |
| $\text{H}_3^+ (\text{H}_2)_{10}$ | -12.80764 | |
| $\text{H}_3^+ (\text{H}_2)_{11}$ | -13.95374 | |