*Chemistry Research Journal*, 2017, 2(2):53-55

*Available online www.chemrj.org*

**Research Article**

**ISSN: 2455-8990**
**CODEN(USA): CRJHA5**

# The real structure of $H_3^+$ is angular

**Robson Fernandes de Farias**

Universidade Federal do Rio Grande do Norte, Cx. Postal 1664, 59078-970 Natal-RN, Brazil

**Abstract** In the present communication, an attempt to clarify what is the real structure of the pivotal interstellar ion $H_3^+$ is conducted. Calculations were performed for three $H_3^+$ structures: the "traditional" equilateral triangular and linear ones, as well as an angular structure. Based on the $G^\theta$ and$S^\theta$ values, it is proposed that the real (most stable) structure for $H_3^+$ is angular, and not equilateral triangular as accepted until now.

**Keywords** $H_3^+$, angular, structure, infrared

## Introduction

The $H_3^+$ ion was discovered by Thomson, in 1911 [1]. In 1961, it was proposed his existence in interstellar space [2] and such existence was indeed detected in 1996 [3]. Since then, a lot of detections have been reportedand subsequent observations have revealed the ubiquity of $H_3^+$ion, which plays the pivotal role in interstellar chemistry [4]. Since the later 1930´s, with the works of Hirschfelder [5] and in the early 1960´s [6,7] it was stablished that the equilateral triangular structure is the most stable for such cation.

Taking into account both, the theoretical and experimental importance of $H_3^+$,as well as the advancements in theory and computational capabilities, I think that some studies involving such chemical specie must be revisited. As will be shown here, the real (most stable) structure for $H_3^+$ is angular and not equilateral triangular as accepted until now.

All calculations were performed by using Spartan´16 [8] (DFT-ωB97X-V/ def2-QZVPPD and Hartree-Fock; 6-311+$G^{**}$ theory levels; optimized geometry at 6-31$G^*$ level).

The calculations were performed on three $H_3^+$ structures: the "traditional" equilateral triangular and linear ones, previously considered [5-7] and an angular one. All modelled structures are shown in Figure 1. For all modelled structures, a zero number of unpaired electrons was considered (ground state structures). The obtained results are summarized in Table 1.

As comparison, a total energy value to the triangular equilateral structure by using an improved Monte Carlo calculation [9] was -1.348835 ± 0.000001 au, a value 132.08 kJmol$^{-1}$ higher than the calculated here.

The triangular geometry belongs to the $D_{3h}$ point group, whereas the angular geometry is $C_{2v}$. For both structures, an IR band at 2859 cm$^{-1}$ and Raman bans at 3540 cm$^{-1}$ and 2859 cm$^{-1}$ were calculated.

The infrared spectra of $H_3^+$ have been the main tool to investigate and identify its presence in planetary and interstellar media. The vibrational-rotational spectra of $H_3^+$ has received a lot of experimental and theoretical attention and more than two hundred band have been assigned for such spectra [10] The calculated IR band at 2859 cm$^{-1}$ is in good relation with those at 2830 cm$^{-1}$ $\nu_2$ emission band detected in Saturn [11].

As can be verified based on Table 1 data, comparing the total energy and $G^\theta$ values to the equilateral triangular and linear structures, it is concluded that the former is the most stable, as previously [5-7] stated.

Furthermore, it is verified that the traditionally accepted equilateral triangular structure cannot, based on the total energy or the energy of the frontiers orbitals, as well as the bond distances, bond angles and bond orders, be differentiated from the proposed angular geometry. Such differentiation cannot also be performed based on the predicted IR and Raman bands.

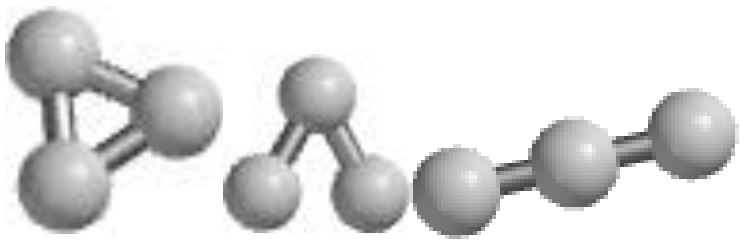
However, two key parameters strongly suggests that the most stable structure for $H_3^+$ is angular and not equilateral triangular as accepted until now: larger $G^\theta$ and $S^\theta$ values to the angular geometry. So, based on these calculated values, it is proposed here that the real (most stable) structure for $H_3^+$ is angular.

It is worth noting that previously [12] (and based on results obtained by topological analysis and quantum mechanical structure) was concluded that "$H_3^+$ is one example of molecules whose quantum mechanical molecular graph are thoroughly different from their classical bond scheme. Therefore this molecule cannot be classified as a ring system on the basis of our results".

**Table 1:** Calculated parameters for $H_3^+$ with different geometries.

| **Parameters/Geometry** | **Triangular** | **Angular** | **Linear** |
|---|---|---|---|
| Point group | $D_{3h}$ | $C_{2v}$ | $D_{\infty h}$ |
| Total energy/au | -1.29852959 | -1.29852953 | -1.22668921 |
| | -1.34245864[a] | -1.34245863[a] | -1.27669477[a] |
| $E_{homo}$/eV | -32.95 | -32.95 | -30.16 |
| $E_{lumo}$/eV | -5.20 | -5.21 | -9.46 |
| Dipole moment/D | 0.00[a] | 0.80[a] | 0.00[a] |
| Polarizability | 36.10 | 36.09 | 37.72 |
| ZPE/kJmol$^{-1}$ | 55.37 | 55.39 | 40.57 |
| $G^\theta$/au | -1.29035910 | -1.29138842 | -1.22570075 |
| $H^\theta$/au | -1.27366416 | -1.27365663 | -1.20698985 |
| $S^\theta$/JK$^{-1}$mol$^{-1}$ | 147.02 | 156.15 | 164.77 |
| $C_v$/ JK$^{-1}$mol$^{-1}$ | 24.95 | 24.95 | 29.11 |
| H-H distance/pm | 86.90 | 86.90 | 80.30 |
| H-H-H angle | 60$^o$ | 60$^o$ | 180$^o$ |
| H-H Mulliken bond order | 0.44 | 0.44 | 0.49 |

[a]Calculated by DFT-ωB97X-V/ def2-QZVPPD.



**(a)** **(b)** **(c)**

*Figure 1: Equilateral triangular (a) angular (b) and linear (c) structures for $H_3^+$*

**References**


[1]. Thomson, J.J.. Rays of positive electricity. *Philos. Mag.*, 1911, *21*, 225-249.

[2]. Martin, D.W.; McDaniel, E.W.; Meeks, M.L., On the possible occurrence of $H_3^+$ in interstellar space, Astrophys. J., 1961, *134*, 1012-1013.

[3]. Gerabelle, T.R.; Oka, T. Detection of $H_3^+$ in interstellar space, Nature, 1996, *384*, 334-335.

[4]. Oka, T. Interstellar $H_3^+$, *PNAS*, 2006, *103*, 12235-12242.

[5]. Hirschfelder, J.O. The energy of the triatomic hydrogen molecule and ion, *J. Chem. Phys*., 1938, *6*, 795-806.
[6]. Christoffersen, R.E.; Hagstrom, S.; Prosser, F. $H_3^+$ molecule ion. Its structure and energy, *J. Chem. Phys*., 1964, *40*, 236-237.
[7]. Conroy, H.Potential Energy Surfaces for the $H_3^+$ Molecule-Ion*J. Chem. Phys*., 1964, *40*, 603-604.
[8]. Wavefunction Inc., Irvine, California, USA, 2016.
[9]. Anderson, J.B., Quantum chemistry by random walk: Higher accuracy for $H^+_3$, *J. Chem. Phys*., 1992, *96*, 3702-3706.
[10]. Dinelli, B.M.; Neale, L.; Polyansky, O.L.; Tennyson, J. New assignments for the infrared spectrum of $H_3^+$, *J. Mol. Spectros*., 1997, *181*, 142-150.
[11]. Oka, T. The infrared spectrum of $H_3^+$ in laboratory and space plasmas, *Rev. Modern Phys*., 1992, *64*, 1141-1149.
[12]. A. Sadjadi, M. Abdzadeh, H. Behnejad, Topological analysis and quantum mechanical structure of $H_3^+$, J. Chem. Res., 5 (2004) 358-359.