To be or not to be: the early history of \( H_3 \) and \( H_3^+ \)

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Triatomic hydrogen became a major research area only after 1980, but its history goes back to J. J. Thomson’s discovery in 1911. In fact, the possible existence of \( H_3 \) was suggested as early as 1895. This paper outlines the history of \( H_3 \) and \( H_3^+ \) up to the mid-1930s, when chemists and physicists ceased to believe in the existence of the \( H_3 \) molecule. In the intervening years, there was a great deal of interest in ‘active hydrogen’ and also in the configuration of \( H_3 \), which was examined by Bohr in 1919. While \( H_3 \) was abandoned, \( H_3^+ \) was not. Although the properties of \( H_3^+ \) were largely unknown, the existence of the ion was firmly established, and its structure studied by means of the new methods of quantum chemistry.

**Keywords:** triatomic hydrogen; active hydrogen; J. J. Thomson; N. Bohr; G. Wendt

1. Triatomic hydrogen in 1895

The triatomic hydrogen ion \( H_3^+ \) grew out of J. J. Thomson’s experiments on positive rays emitted in discharge tubes. These rays, also known as canal rays, were discovered by the German physicist Eugen Goldstein in 1886 and subsequently investigated in great detail by his compatriot Wilhelm Wien [1]. A leader in the study of *Kanalstrahlen* (and a Nobel laureate of 1912), Wien accepted Thomson’s discovery not only of \( H_3^+ \) but also of the neutral \( H_3 \) molecule.

The generally held belief that the stories of \( H_3^+ \) and \( H_3 \) have their beginnings in Thomson’s experiments is not quite justified. More than 15 years earlier, one can find in the chemical literature references to the possible existence of \( H_3 \), which a few scientists thought might represent the newly discovered helium gas. Originally hypothesized to be a solar element, in 1895, He was unexpectedly found in terrestrial minerals [2]. The peculiar double structure of its spectrum seemed to indicate that there were two species of He: the ordinary one (with an atomic weight of about 5) and ‘parhelium’ (with an atomic weight of 3) [3]. The recognized Czech chemist Bohuslav Brauner thought that parhelium might be an allotropic form of hydrogen, \( H_3 \), that is structurally similar to ozone, \( O_3 \) [4,5]. His hypothesis was short-lived and considered only by a few scientists. With

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the recognition that there is only one kind of helium, albeit with two different systems of spectral series, Brauner’s hypothesis was forgotten. There is no reason to believe that Thomson knew of it.

2. J. J. Thomson: experiments and interpretations

By the early 1910s, Joseph John Thomson was Britain’s most distinguished physicist. Following his discovery of the electron in 1897, he developed an ambitious theory of the atom, which, for nearly a decade, was considered the best candidate for the internal structure of atoms [6]. However, the original Thomson model soon ran into trouble, primarily because it was realized that the number of electrons in atoms was only of the order of the atomic weight. This forced him to take the positive charge more seriously than he had done previously (when he thought of the positive charge as a massless fluid smeared out over the entire volume of the atom). It was in this context that he embarked on an extensive experimental research programme with the aim of investigating positive rays in discharge tubes, a line of research he cultivated from about 1908 to 1914 [7,8].

During his experiments with electric and magnetic deflections of positive rays, he noted an ‘X3’ component that had a mass-to-charge ratio three times that of the hydrogen atomic ion,

$$\left(\frac{m}{e}\right)_{X_3} = 3 \left(\frac{m}{e}\right)_{H^+}.$$

The result might have been due to a C4+ ion, but Thomson found it more likely that the component was H3+, a hypothesis he first stated in the February 1911 issue of *Philosophical Magazine* [9]. Over the next few years, he substantiated the hypothesis, which he presented at various scientific meetings and described in detail in a monograph of 1913, *Rays of Positive Electricity* [7].

According to Thomson, not only had he discovered a new molecular ion, H3+, he had also discovered the neutral molecule H3. Although he was unable to obtain a spectrum of the new and elusive gas, he was convinced that it existed in a stable form. Remarkably, it appeared to be almost chemically inert and resistant to decomposition by electric discharges. ‘X3 seems more stable than any known allotropic form of an element’, he pointed out [7, p. 122]. Although Thomson abandoned his research programme on positive rays in 1914, 20 years later he returned to it, repeating his belief in a permanent form of H3. Looking back on his early experiments, the 78 year old physicist wrote that the H3 particles occurred with great regularity when certain solids such as KOH were bombarded by cathode rays. ‘The H3 I obtained from this source was a permanent gas’, he stated [10, p. 1026].

Well aware that a triatomic hydrogen molecule conflicted with ordinary ideas of valence, Thomson nonetheless suggested that a triangular form of the molecule might agree with modern theories of atomic structure. After all, in the early 1910s, the chemical theory of valence was empirical and lacked support from atomic theory. Using his favoured name ‘corpuscle’ for the electron, in 1913 he suggested to ‘regard an atom of hydrogen as consisting of a positive nucleus and one negative corpuscle’, in which case he saw ‘no reason why a group of three of these arranged so that their axes form a closed ring should not form a stable arrangement’ [7, p. 121]. The quotation might indicate that Thomson at that
time accepted Ernest Rutherford’s nuclear atom, but this was not the case. The ‘positive nucleus’ did not refer to Rutherford’s tiny central charge, but to the inner part of the atom, which he conceived as an arrangement of concentric layers of positive and negative electrons governed by attractive and repulsive forces, some of them known and others unknown.

3. Theoretical intermezzo

Niels Bohr stayed with Thomson as a postdoctoral fellow in Cambridge, UK, from September 1911 to March 1912, after which he moved on to Manchester, UK, to work under Rutherford (who had himself been with Thomson as a postdoctoral fellow). Shortly after having published his seminal paper on atomic theory in the summer of 1913, Bohr attended the meeting of the British Association for the Advancement of Science in Birmingham, UK. In the discussion session following a talk Thomson gave on his X$_3 = H_3$ hypothesis, the young Dane suggested as an alternative that X$_3$ might be a super-heavy isotope of hydrogen rather than a molecule. (At that time, the name ‘isotope’ had not yet been coined.) Nearly 50 years later, Bohr recalled: ‘I just took up the question of whether in hydrogen one could have what you now call tritium. And then I saw that it was a way to show this by its diffusion in palladium. Hydrogen and tritium will behave similarly but the masses are so different that they will get separated out’ (interview with N. Bohr of 1 November 1962, American Institute of Physics transcript; http://www.aip.org/history/ohilist/4517_1.html).

Bohr’s suggestion was not taken seriously, but, after having returned to Copenhagen, Denmark, he continued to think about it, realizing that in principle the question might be resolved by spectroscopic precision experiments. According to his theory of one-electron atoms, Rydberg’s constant $R$ would vary with the reduced mass and the wavelengths thus depend on the mass of the nucleus. In the case of tritium (T) and ordinary hydrogen (H), the difference in wavelength would be

$$\Delta \lambda = \lambda_H \left(1 - \frac{R_H}{R_T}\right) \approx 3.6 \times 10^{-5} \lambda_H,$$

which Bohr thought was ‘of an order open for detection’. However, experiments made in Copenhagen failed to disclose the isotope effect, which was established only for hydrogen isotopes when deuterium was discovered in 1932.

In 1919, in a little known paper published by the Nobel Institute in Stockholm, Sweden [11], Bohr examined theoretically the H$_3$ molecule, which he assumed consisted of three electrons rotating in a circular orbit around the nucleus in the middle of the system (figure 1). Having concluded that the system was mechanically stable, he suggested a mechanism that would allow an ionized H$_2$ gas to form H$_3$ in spite of the direct process $3H_2 \rightarrow 2H_3$ being endothermic. His theoretical investigation focused on H$_3$ rather than on H$_3^+$, the reason being that for the latter system ‘no configuration of mechanical equilibrium … can be formed’. If an electron were removed from H$_3$, the ion would split up according to

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

On the other hand, Bohr’s calculations showed that H$_3$ could add one more electron and form a stable H$_3^-$ ion, which he predicted ‘may exist permanently
in the absence of external agencies'. Of course, his theoretical results ran counter to Thomson’s experimental detection of $\text{H}_3^+$ (and the absence of $\text{H}_3^-$), but Bohr thought that the disagreement might only be apparent: perhaps the decay of the $\text{H}_3^+$ ions was somehow delayed under the conditions governing Thomson’s experiments.

Bohr did not follow up his paper of 1919, which was not well known and had little effect on later research. Neither did other atomic physicists in the tradition of the old Bohr–Sommerfeld quantum theory feel tempted to analyse the hypothetical molecule. The only prominent physicist, apart from Thomson and Bohr, who supported the existence of $\text{H}_3$ was Johannes Stark in Germany [12]. In 1913—the same year he discovered the spectroscopic Stark effect—he proposed a triangular model of $\text{H}_3$ similar to the one suggested by Thomson (figure 2). Stark also endorsed the claim of $\text{H}_3^+$, but his work in the area of hydrogen molecules and ions had even less impact than Bohr’s.

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Figure 3. Experiment of 1925 showing the existence of the H$_3^+$ ion [15].

4. H$_3^+$ vindicated

Whereas the question of neutral H$_3$ evolved into a muddled controversy, the existence of the positive ion was never seriously contested. Not only were Thomson’s experiments and interpretations widely accepted, evidence in support of H$_3^+$ was also provided by many later researchers. Thus, in experiments with positive hydrogen rays of 1916, the Canadian–American physicist Arthur Dempster confirmed the presence of H$_3^+$ in addition to the known ions H$^+$ and H$_2^+$. Contrary to Thomson, Dempster did not regard either H$_3^+$ or H$_3$ as a stable gas, ‘since it is not present when there is no dissociation of the hydrogen molecules’ [13]. Whereas, in one of his papers of 1916 [14], Dempster suggested the formation process H$^+$ + H$_2$ $\rightarrow$ H$_3^+$, in another [13] he concluded as follows: ‘Electrons ... ionize hydrogen by detaching a single elementary charge from the molecule. They are not able to dissociate the gas. The positive molecules so formed are able to dissociate the gas. When this occurs, the complex H$_3^+$ is formed.’

American and German physicists applied improved versions of Dempster’s ionization method to extend his results and suggest mechanisms for the production of H$_3^+$ (figure 3). In 1924, Thorfin R. Hogness and E. G. Lunn, two chemists at the University of California, suggested that H$_3^+$ was produced in a secondary process, H$^+$ + H$_2$ $\rightarrow$ H$_3^+$, the primary process being H$_2$ $\rightarrow$ H + H$^+$ + e$^-$ [16]. The following year they retracted their suggestion, now concluding that ‘the formation of H$_3^+$ is the primary process, and ... H$^+$ and H$_3^+$ are formed from H$_2^+$ as the result of secondary collisions with gas molecules’ [17]. They assumed H$_2^+$ to be metastable, colliding with a H$_2$ molecule according to H$_2$ + H$_2^+$ $\rightarrow$ H$_3^+$ + H.

This was the same process that Dempster had proposed in 1916, if less detailed and in words only. Hogness and Lunn also considered the reaction H$_2^+$ $\rightarrow$ H + H$^+$ followed by H$^+$ + H$_2$ $\rightarrow$ H$_3^+$, but argued that these processes occurred much less frequently. In a slightly earlier paper, the Princeton physicist Henry DeWolf Smyth [15] had also discussed the formation of H$_3^+$, including the possibilities...
H^+ + H_2 \rightarrow H_3^+ \text{ and } H^+ + H_2^+ \rightarrow H_3^+. \text{ However, he did not suggest the main reaction proposed a few months later by Hogness and Lunn, which was confirmed by Gaylord Harnwell and other researchers [18].}

A most convincing demonstration of H_3^+ was produced when Kenneth Bainbridge at the Franklin Institute, Swarthmore, PA, and later Overton Luhr at Union College, Schenectady, NY, detected the ion in the mass spectrum of hydrogen isotopes [19,20]. One of Luhr’s spectra is shown in figure 4. The spectroscopic discovery of deuterium gave rise to some new research on H_3^+. Two physical chemists in Berlin, Germany, Hartmut Kallmann and W. Lasareff, looked in vain for a hydrogen compound of mass 4, supposed to be D_2^+ or H_2D^+, but they succeeded in detecting HD^+ in their mass spectrograph [21,22]. They concluded that H_2D^+ must be extremely rare compared with H_3^+. However, Bainbridge found lines in his mass-spectrographic measurements that corresponded to a mass of 4.0285 and which he attributed to H_2D^+ [23]. In experiments from 1933, he reported the detection of more hydrogen molecular ions, including H_3^{2+}, D_2H^+ and D_3^+ [24].

In spite of the generally held belief in H_3^+, the situation in the 1920s was not entirely satisfactory: although the ion turned up as an experimental signal, almost nothing was known of its properties or molecular constitution. Several groups of scientists looked for the spectrum of H_3^+, yet nothing came out of their efforts. In view of the much later development, it is of interest to recall that young Gerhard Herzberg, at the time a doctoral student at Darmstadt Technische Hochschule in Germany, dealt with the subject in his dissertation of 1927 [25]. A study of the so-called secondary spectrum of hydrogen led Smyth and his collaborator Charles

Figure 4. Mass spectrum of 1935, showing ions in a hydrogen mixture with 16% deuterium [20].
Brasefield [26] to the tentative conclusion that they had found spectroscopic evidence for $H_3^+$, but the evidence was indirect and not generally considered convincing. Although the triatomic hydrogen ion was accepted by the early 1930s, it remained an open question what it was, more precisely.

If experiments could not yield an answer, perhaps theory could. This, at any rate, was the philosophy of the first-generation quantum chemists who, in the 1930s, applied their computational methods to simple molecules such as $H_2$ and $H_3^+$. Thus, Charles Coulson at the University of Cambridge concluded that, while $H_3^+$ in its ground state existed in the form of an equilateral triangle, the excited states would be unstable [27]. Also according to Joseph Hirschfelder, a physical chemist at the University of Wisconsin, the triangular structure was more stable than the linear structure. He concluded after lengthy calculations that the $H_3^+$ ion had a stable configuration corresponding to a separation between the nuclei of about 1.79 Å with the nuclei lying intermediate between a right and an equilateral triangle [28]. For the reaction $H_2 + H_2^+ \rightarrow H_3^+ + H$, he found that it was exothermic by 40 kcal mol$^{-1}$. Moreover, he estimated the vibration frequencies of the equilateral form of $H_3^+$, finding that ‘the z and y modes of vibration should be infra-red and therefore susceptible to direct experimental observation’. The remark was potentially important, but it was not followed up and did not lead to an experimental search for the spectral lines.

5. A chemical enigma

The question of the neutral $H_3$ molecule turned out to be much more complex and controversial than Thomson had anticipated [29]. Following a work by William Duane and Gerald Wendt in 1917 [30], over the next decade several chemists and physicists claimed to have produced evidence for a new reactive form of hydrogen that most likely was $H_3$. Francis Aston, inventor of the mass spectrograph and a former assistant to Thomson, was among those who supported the case of the $H_3$ molecule, the mass of which he determined to be 3.025 atomic mass units (compared with $H$ = 1.008). In the second edition of his book *Isotopes*, he wrote about triatomic hydrogen: ‘The mass deduced proves in a conclusive manner that the particle causing it [the mass-3 parabola] is a molecule of three hydrogen atoms’ [31, p. 70].

The Duane–Wendt paper of 1917 introduced effectively the hypothesis of ‘active hydrogen’, a polyatomic form with unusual properties that, in most cases, was identified with $H_3$. According to the two Americans, the new gas was probably a hydrogenic version of ozone, a proposal Wendt elaborated on in a later paper written with his student Robert Landauer [32]:

the properties of the new gas are precisely those to be expected of an ozone form. ... Its boiling point is much higher than that of ordinary hydrogen. And it is unstable, for it cannot be detected if more than about a minute is allowed to elapse between the time of its formation and its reaction with a reducible substance. All the evidence obtained, then, points to the formation of triatomic hydrogen, perhaps properly called ‘hyzone’, when ever hydrogen is ionized.

The name ‘hyzone’ or the German equivalent ‘Hyzon’ never caught on. It was occasionally used in the 1920s and 1930s, but today it is nothing but a historical curiosity [33].

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Wendt and most other protagonists of H$_3$ agreed that the new gas was unstable, and perhaps very much so. Many researchers estimated its lifetime to be of the order of 1 min, but there were also suggestions of the much shorter lifetime $3 \times 10^{-8}$ s, the same order as the lifetime of ordinary excited molecules [34]. As to the experimental evidence cited in favour of H$_3$, the following were widely discussed:

— Under the action of alpha rays on pure hydrogen, the volume of the gas contracted. This might indicate a partial transformation of diatomic to triatomic hydrogen: $3\text{H}_2 \rightarrow 2\text{H}_3$.

— The boiling point of active hydrogen was much higher (approx. 70 K) than ordinary hydrogen.

— The new gas combined readily with nitrogen to form ammonia. A possible reaction mechanism was two successive collisions of the N$_2$ molecule with H$_3$ groups, $(\text{N}_2 + \text{H}_3) + \text{H}_3 \rightarrow 2\text{NH}_3$, such as proposed by the Canadian chemist Audrey Grubb [35].

— Active hydrogen formed H$_2$S when passing over unheated sulphur powder.

By the early 1920s, the new H$_3$ gas seemed to be on its way to recognition, but 10 years later, the situation had changed. Grubb and a few others maintained faith in the existence of H$_3$, and as late as 1935 he provided ‘new evidence for the existence of an active form of hydrogen that differs markedly in its properties from atomic hydrogen’ [36]. He suggested that the best candidate for the active form was H$_3$. To my knowledge, this was the last time the H$_3$ hypothesis was defended in the scientific literature until it was revived much later.

6. ‘Triatomic hydrogen does not exist’

From about 1925, an increasing number of chemists and physicists questioned the existence of H$_3$ in the form of active hydrogen. Together with the missing spectroscopic evidence, the accumulation of experimental arguments against the elusive molecule had the effect that neutral triatomic hydrogen lost its credibility. It was downgraded from ‘likely’ to ‘most unlikely’.

What can reasonably be called the campaign against H$_3$ started in 1925 with a series of objections raised by the Russian chemist Abraham Bach, and a few years later they were reinforced by Fritz Paneth in Austria, Harold Urey in the USA, and several other chemists [29]. Paneth concluded that the effects ascribed to H$_3$ could in almost all cases be explained by the presence of traces of H$_2$S in the ‘active’ hydrogen gas [37]. According to Urey and his student Hugh Smallness, many of the experiments that had been used in support of H$_3$ were poor and could not even be reproduced [38]. For example, careful dilatometric measurements failed to produce a contraction effect comparable to the one reported by Wendt and his collaborators. Other precision experiments indicated that the formation of small amounts of NH$_3$ and H$_2$S could be explained without assuming any formation of active hydrogen. In 1931 G. R. Schulze at the University of Minnesota concluded in plain words what many of his colleagues had phrased more cautiously: ‘Triatomic hydrogen does not exist. . . . The non-existence of triatomic hydrogen has been definitely settled’ [39].
It should be noted that the $H_3$ hypothesis was not disproved in any strict sense, but that its credibility was eroded to such an extent that scientists lost interest in it. Indeed, the hypothesis is an example of what philosophers call an existential statement: while one can prove or verify such a statement, how can it possibly be disproved? It is also worth pointing out that the critics aimed their fire only at the neutral $H_3$ molecule. None of them denied the existence of $H_3^+$ in discharge tubes.

Finally, in regard to the later development, it is worth noting that, in the period from 1911 to the late 1930s, there were no suggestions that $H_3$ or $H_3^+$ might be of any interest to the astronomers. The chemical composition of the higher strata of the atmosphere was at the time a disputed issue, not least in connection with the origin of the colours of the aurora borealis [40]. While none of the auroral researchers referred to the possible existence of $H_3$ or $H_3^+$ in the upper atmosphere, in 1923 a French meteorologist hypothesized that certain phenomena of atmospheric low pressure might be due to the $3H_2 \rightarrow 2H_3$ contraction effect argued by Wendt and others [41]. This seems to have been the only suggestion that triatomic hydrogen might play a role outside the laboratory.

7. Concluding remarks

The case of the early history of triatomic history is of interest not only for historical reasons but also because it illustrates certain general features in the scientific process. First of all, it is a nice example of the evidential nature of scientific knowledge. Second, it problematizes the notion of discovery. As far as the question of $H_3$ was concerned, it was all a matter of weighing experimental evidence for and against the hypothesis of $H_3$ as the source of active hydrogen. For a period in the early 1920s, the $H_3$ gas was ‘almost discovered’, in the sense that its existence was considered plausible by a large part of the scientific community. Yet, evidence claims can always be questioned, or they can be challenged by counterevidence, and this is what happened. By the late 1930s, $H_3$ had effectively been de-discovered—only to be re-discovered some 40 years later! That happened when Herzberg unexpectedly found spectral lines from discharge tubes that he attributed to Rydberg states of $H_3$ [42]. One may similarly reflect on the discovery history of $H_3^+$, a molecular ion that apparently was discovered twice, by Thomson in 1911 and by Takeshi Oka in 1980 [43,44]. Moreover, the discoveries of Herzberg and Oka were closely intertwined, as they both occurred in searches for the $H_3^+$ spectrum at the Herzberg Institute of Astrophysics in Ottawa, Canada. On the occasion of Oka’s 60th birthday, Herzberg (at the age of 88) referred to Oka’s first observation of the $H_3^+$ spectrum as the foremost example of his ‘extraordinary persistence … and imagination’ [45]. While Herzberg’s discovery was serendipitous, Oka’s was not.

There is also a historiographical aspect of the case presented here. Together with other cases of a similar nature, it exemplifies ‘presentism’, which is a natural element in much writing of history. Historians deal with the past, and what happened in the past cannot possibly be affected by the present. Nonetheless, our perspective on the past and the significance of past events can and often do depend on the later situation. The main reason why the early history of triatomic hydrogen is of more than antiquarian interest is that $H_3^+$ plays such an important
role in modern research [46]. Had this not been the case, the early history would have appeared much less interesting (and irrelevant to modern scientists) and possibly not worth investigating in any detail.

References

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