

## CORRIGENDUM

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# Correction and addendum to Oka 2000: introductory remarks

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My earlier assignment of the  $H_3^+$  signal in J. J. Thomson's plate is corrected. The double nature of the  $m/e=3$  signal, one due to  $H_3^+$  and the other to  $HD^+$ , which puzzled Thomson for over 20 years, is discussed.

**Keywords:** J. J. Thomson;  $H_3^+$ ;  $HD^+$ ; historical

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The assignment of the  $H_3^+$  signal in J. J. Thomson's plate (Fig. 1 of Oka 2000), which was copied from my earlier review (Oka 1983), was incorrect. The assignment was based on Fig. 21a of Thomson (1912), which is reproduced here as figure 1. Thomson's remark on page 241 'the line is the one marked *a*; above it are the lines due to the hydrogen atom and molecule,' led me to assign the weak parabola pointing towards *a* as  $H_3^+$ , although it was puzzling that it is so far away from the parabolas of  $H^+$  and  $H_2^+$ . Further reading of Thomson's papers and books has revealed that the mark *a* is misplaced and that the  $H_3^+$  signal is the faint dot just below the strongest  $H_2^+$  parabola (shown by an arrow in figure 1).

The  $H_3^+$  signals observed in hydrogen plasmas were often not reproducible and Thomson later called it 'capricious', 'fugitive' or 'evanescent' (Thomson 1934*a-c*, 1937). Thomson's quest to obtain a more 'permanent'  $m/e=3$  signal led him to a different method of producing the '3' line by bombarding solids with cathode rays and using the evaporated gas for discharges. An example of the more permanent '3' line produced by this method is given in Fig. 50 of Thomson (1913*a*) which is reproduced here as figure 2: the '3' line is sandwiched between the  $H_2^+$  and  $He^+$  lines. Thomson spent 8 pages of his 20 page Bakerian Lecture (1931*b*) on how this permanent '3' line was produced by bombarding a great many metals, salts,

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One contribution of 26 to a Discussion Meeting Issue 'Physics, chemistry and astronomy of  $H_3^+$ '.

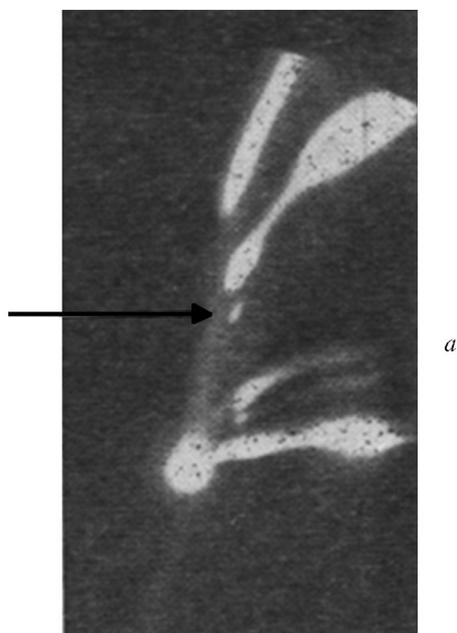


Figure 1. The ‘capricious’  $\text{H}_3^+$  signal. From Thomson (1912).

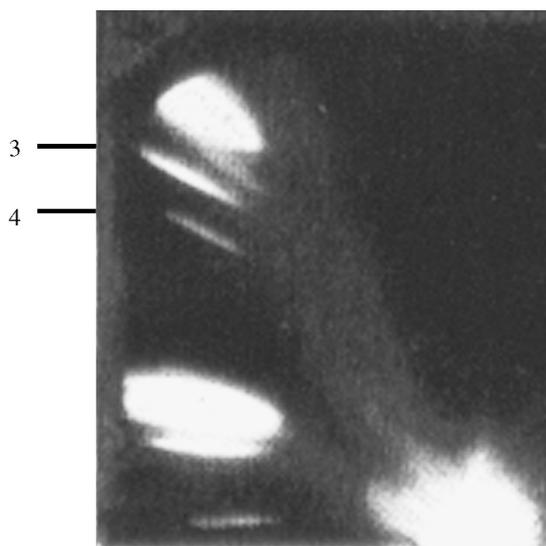


Figure 2. The ‘permanent’ signal later found to be due to  $\text{HD}^+$ . From Thomson (1913a).

meteorites, etc. (26 solids were used!) The existence of the two different kinds of the ‘3’ line puzzled Thomson so much that after the initial two papers (Thomson 1911, 1912), he refrained from using  $\text{H}_3^+$  and used  $\text{X}_3$  instead, in his papers and books.

After 20 years, Thomson’s quandary was finally resolved when the deuterium was discovered by Urey, Brickwedde and Murphy in 1932. After repeating the experiment using ‘samples of 80 per cent concentration of heavy hydrogen’ obtained ‘through the kindness of Lord Rutherford’, Thomson understood that

the capricious, fugitive and evanescent signal of figure 1 was indeed due to  $\text{H}_3^+$ , but the permanent signal in figure 2 was  $\text{HD}^+$  due to HD desorbed from the solids. This led to his somewhat misleading remark (Thomson 1934a), ‘The evidence seems to me to leave little doubt that the gas I called  $\text{H}_3$  more than 20 years ago is the same as that which is now called heavy hydrogen’. The properties of the dot signal due to  $\text{H}_3^+$  were discussed in Thomson (1935), although some explanations are cryptic.

Thomson’s last remark on  $\text{H}_3^+$  appeared in his autobiography (Thomson 1937) where he convincingly writes ‘one of the first things discovered by the photographic method was the existence of  $\text{H}_3^+$ ’. However, his later remark in the same book, ‘though  $\text{H}_3^+$  is so evanescent,  $\text{H}_3$  itself is much more durable, for when  $\text{H}_3$  has once been observed in a tube, then though the tube has not been sparked for several days,  $\text{H}_3^+$  will at once appear when sparking is resumed’, indicates that Thomson had not understood the chemistry of  $\text{H}_3^+$ . The secondary nature of the  $\text{H}_3^+$  production, i.e. ionization of  $\text{H}_2$  to  $\text{H}_2^+$  followed by the reaction  $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ , was left to younger generation of American scientists, Dempster, Hogness and Smyth, to figure out (Oka 1983, 2000).

I am indebted to B. J. McCall for initiating discussions leading to this clarification.

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