

																		1	2	3																		
																		H	He																			
4	5																	6	7	8	9	10																
Li	Be																	B	C	N	O	F	Ne															
11	12																	13	14	15	16	17	18															
Na	Mg																	Al	Si	P	S	Cl	Ar															
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36																					
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Cu	Ni	Zn	Ga	Ge	As	Se	Br	Kr																						
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																					
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																					
55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72																					
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu																						
87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104																					
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr																						

# 3

## Hydrogen

### 3.1 Introduction

Hydrogen is the most abundant element in the universe and is also common on earth, being the third most abundant element (after oxygen and silicon) on the surface of the globe. Hydrogen in combined form accounts for about 15.4% of the atoms in the earth's crust and oceans and is the ninth element in order of abundance by weight (0.9%). In the crustal rocks alone it is tenth in order of abundance (0.15 wt%). The gradual recognition of hydrogen as an element during the sixteenth and seventeenth centuries forms part of the obscure and tangled web of experiments that were carried out as chemistry emerged from alchemy to become a modern science.<sup>(1)</sup> Until almost the end of the eighteenth century the element was inextricably entwined with the concept of phlogiston and H. Cavendish, who is generally regarded as having finally isolated and identified the gas in 1766, and who established conclusively that water was a compound of

oxygen and hydrogen, actually communicated his findings to the Royal Society in January 1784 in the following words: "There seems to be the utmost reason to think that dephlogisticated air is only water deprived of its phlogiston" and that "water consists of dephlogisticated air united with phlogiston".

The continued importance of hydrogen in the development of experimental and theoretical chemistry is further illustrated by some of the dates listed in the Panel on the page opposite.

Hydrogen was recognized as the essential element in acids by H. Davy after his work on the hydrohalic acids, and theories of acids and bases have played an important role ever since. The electrolytic dissociation theory of S. A. Arrhenius and W. Ostwald in the 1880s, the introduction of the pH scale for hydrogen-ion concentrations by S. P. L. Sørensen in 1909, the theory of acid-base titrations and indicators, and J. N. Brønsted's fruitful concept of acids and conjugate bases as proton donors and acceptors (1923) are other land marks (see p. 48). The discovery of *ortho*- and *para*-hydrogen in 1924, closely followed by the discovery of heavy hydrogen (deuterium) and

<sup>1</sup> J. W. MELLOR, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 1, Chap. 3, Longmans, Green & Co., London, 1922.

tritium in the 1930s, added a further range of phenomena that could be studied by means of this element (pp. 34–43). In more recent times, the technique of nmr spectroscopy, which was first demonstrated in 1946 using the hydrogen nucleus, has revolutionized the study of structural chemistry and permitted previously unsuspected

phenomena such as fluxionality to be studied. Simultaneously, the discovery of complex metal hydrides such as  $\text{LiAlH}_4$  has had a major impact on synthetic chemistry and enabled new classes of compound to be readily prepared in high yield (p. 229). The most important compound of hydrogen is, of course, water,

### Hydrogen — Some Significant Dates

- 1671 R. Boyle showed that dilute sulfuric acid acting on iron gave a flammable gas; several other seventeenth-century scientists made similar observations.
- 1766 H. Cavendish established the true properties of hydrogen by reacting several acids with iron, zinc and tin; he showed that it was much lighter than air.
- 1781 H. Cavendish showed quantitatively that water was formed when hydrogen was exploded with oxygen, and that water was therefore not an element as had previously been supposed.
- 1783 A. L. Lavoisier proposed the name "hydrogen" (Greek ὕδωρ γείνομαι, water former).
- 1800 W. Nicholson and A. Carlisle decomposed water electrolytically into hydrogen and oxygen which were then recombined by explosion to resynthesize water.
- 1810–15 Hydrogen recognized as the essential element in acids by H. Davy (contrary to Lavoisier who originally considered oxygen to be essential — hence Greek ὀξύς γείνομαι, acid former).
- 1866 The remarkable solubility of hydrogen in palladium discovered by T. Graham following the observation of hydrogen diffusion through red-hot platinum and iron by H. St. C. Deville and L. Troost, 1863.
- 1878 Hydrogen detected spectroscopically in the sun's chromosphere (J. N. Lockyer).
- 1895 Hydrogen first liquefied in sufficient quantity to show a meniscus (J. Dewar) following earlier observations of mists and droplets by others, 1877–85.
- 1909 The pH scale for hydrogen-ion concentration introduced by S. P. L. Sørensen.
- 1912  $\text{H}_3^+$  discovered mass-spectrometrically by J. J. Thompson.
- 1920 The concept of hydrogen bonding introduced by W. M. Latimer and W. H. Rodebush (and by M. L. Huggins, 1921).
- 1923 J. N. Brønsted defined an acid as a species that tended to lose a proton:  $\text{A} \rightleftharpoons \text{B} + \text{H}^+$ .
- 1924 *Ortho*- and *para*-hydrogen discovered spectroscopically by R. Mecke and interpreted quantum-mechanically by W. Heisenberg, 1927.
- 1929–30 Concept of quantum-mechanical tunnelling in proton-transfer reactions introduced (without experimental evidence) by several authors.
- 1931 First hydrido complex of a transition metal prepared by W. Hieber and F. Leutert.
- 1932 Deuterium discovered spectroscopically and enriched by gaseous diffusion of hydrogen and by electrolysis of water (H. C. Urey, F. G. Brickwedde and G. M. Murphy).
- 1932 Acidity function  $\text{H}_0$  proposed by L. P. Hammett for assessing the strength of very strong acids.
- 1934 Tritium first made by deuteron bombardment of  $\text{D}_3\text{PO}_4$  and  $(\text{ND}_4)_2\text{SO}_4$  (i.e.  ${}^2\text{D} + {}^2\text{D} = {}^3\text{T} + {}^1\text{H}$ ); M. L. E. Oliphant, P. Harteck and E. Rutherford.
- 1939 Tritium found to be radioactive by L. W. Alvarez and R. Cornog after a prediction by T. W. Bonner in 1938.
- 1946 Proton nmr first detected in bulk matter by E. M. Purcell, H. C. Torrey and R. V. Pound; and by F. Bloch, W. W. Hansen and M. E. Packard.
- 1947  $\text{LiAlH}_4$  first prepared and subsequently shown to be a versatile reducing agent; A. E. Finholt, A. C. Bond and H. I. Schlesinger.
- 1950 Tritium first detected in atmospheric hydrogen (V. Faltings and P. Harteck) and later shown to be present in rain water (W. F. Libby *et al.*, 1951).
- 1954 Detonation of the first hydrogen bomb on Bikini Atoll.
- 1960s "Superacids" ( $10^7$ – $10^{19}$  times stronger than sulfuric acid) studied systematically by G. A. Olah's group and by R. J. Gillespie's group.
- 1966 The term "magic acid" coined in G. A. Olah's laboratory for the non-aqueous system  $\text{HSO}_3\text{F}/\text{SbF}_5$ .
- 1976–79 Encapsulated H atom detected and located in octahedral polynuclear carbonyls such as  $[\text{HRu}_6(\text{CO})_{18}]^-$  and  $[\text{HCo}_6(\text{CO})_{15}]^-$  following A. Simon's characterization of interstitial H in  $\text{HNb}_6\text{I}_{11}$ .
- 1984 Stable transition-metal complexes of dihapto-dihydrogen ( $\eta^2\text{-H}_2$ ) discovered by G. Kubas.

and a detailed discussion of this compound is given on pp. 620–33 in the chapter on oxygen. In fact, hydrogen forms more chemical compounds than any other element, including carbon, and a survey of its chemistry therefore encompasses virtually the whole periodic table. However, before embarking on such a review in Sections 3.4–3.7 it is convenient to summarize the atomic and physical properties of the various forms of hydrogen (Section 3.2), to enumerate the various methods used for its preparation and industrial production, and to indicate some of its many applications and uses (Section 3.3).

## 3.2 Atomic and Physical Properties of Hydrogen<sup>(2)</sup>

Despite its very simple electronic configuration ( $1s^1$ ) hydrogen can, paradoxically, exist in over 50 different forms most of which have been well characterized. This multiplicity of forms arises firstly from the existence of atomic, molecular and ionized species in the gas phase: H, H<sub>2</sub>, H<sup>+</sup>, H<sup>-</sup>, H<sub>2</sub><sup>+</sup>, H<sub>3</sub><sup>+</sup> . . . , H<sub>11</sub><sup>+</sup>; secondly, from the existence of three isotopes, <sup>1</sup>H, <sup>2</sup>H(D) and <sup>3</sup>H(T), and correspondingly of D, D<sub>2</sub>, HD, DT, etc.; and, finally, from the existence of nuclear spin isomers for the homonuclear diatomic species,

<sup>2</sup> K. M. MACKAY, The element hydrogen, *Comprehensive Inorganic Chemistry*, Vol. 1, Chap. 1. K. M. MACKAY and M. F. A. DOVE, Deuterium and tritium, *ibid.*, Vol. 1, Chap. 3, Pergamon Press, Oxford, 1973.

i.e. *ortho*- and *para*-dihydrogen, -dideuterium and -ditritium.<sup>†</sup>

### 3.2.1 Isotopes of hydrogen

Hydrogen as it occurs in nature is predominantly composed of atoms in which the nucleus is a single proton. In addition, terrestrial hydrogen contains about 0.0156% of deuterium atoms in which the nucleus also contains a neutron, and this is the reason for its variable atomic weight (p. 17). Addition of a second neutron induces instability and tritium is radioactive, emitting low-energy  $\beta^-$  particles with a half-life of 12.33 y. Some characteristic properties of these 3 atoms are given in Table 3.1, and their implications for stable isotope studies, radioactive tracer studies, and nmr spectroscopy are obvious.

In the molecular form, dihydrogen is a stable, colourless, odourless, tasteless gas with a very low mp and bp. Data are in Table 3.2 from which it is clear that the values for deuterium and tritium are substantially higher.

<sup>†</sup> The term dihydrogen (like dinitrogen, dioxygen, etc.) is used when it is necessary to refer unambiguously to the molecule H<sub>2</sub> (or N<sub>2</sub>, O<sub>2</sub>, etc.) rather than to the element as a substance or to an atom of the element. Strictly, one should use "diprotium" when referring specifically to the species H<sub>2</sub> and "dihydrogen" when referring to an undifferentiated isotopic mixture such as would be obtained from materials having the natural isotopic abundances of H and D; likewise "proton" only when referring specifically to H<sup>+</sup>, but "hydron" when referring to an undifferentiated isotopic mixture.

**Table 3.1** Atomic properties of hydrogen (protium), deuterium, and tritium

Property	H	D	T
Relative atomic mass	1.007 825	2.014 102	3.016 049
Nuclear spin quantum number	$\frac{1}{2}$	1	$\frac{1}{2}$
Nuclear magnetic moment/(nuclear magnetons) <sup>(a)</sup>	2.792 70	0.857 38	2.978 8
NMR frequency (at 2.35 tesla)/MHz	100.56	15.360	104.68
NMR relative sensitivity (constant field)	1.000	0.009 64	1.21
Nuclear quadrupole moment/( $10^{-28}$ m <sup>2</sup> )	0	$2.766 \times 10^{-3}$	0
Radioactive stability	Stable	Stable	$\beta^-$ $t_{\frac{1}{2}}$ 12.33 y <sup>(b)</sup>

<sup>(a)</sup> Nuclear magneton  $\mu_N = eh/2m_p = 5.0508 \times 10^{-27}$  J T<sup>-1</sup>.

<sup>(b)</sup>  $E_{\max}$  18.6 keV;  $E_{\text{mean}}$  5.7 keV; range in air  $\sim 6$  mm; range in water  $\sim 6 \mu\text{m}$ .

Table 3.2 Physical properties of hydrogen, deuterium and tritium

Property <sup>(a)</sup>	H <sub>2</sub>	D <sub>2</sub>	T <sub>2</sub>
MP/K	13.957	18.73	20.62
BP/K	20.39	23.67	25.04
Heat of fusion/kJ mol <sup>-1</sup>	0.117	0.197	0.250
Heat of vaporization/kJ mol <sup>-1</sup>	0.904	1.226	1.393
Critical temperature/K	33.19	38.35	40.6 (calc)
Critical pressure/atm <sup>(b)</sup>	12.98	16.43	18.1 (calc)
Heat of dissociation/kJ mol <sup>-1</sup> (at 298.2 K)	435.88	443.35	446.9
Zero point energy/kJ mol <sup>-1</sup>	25.9	18.5	15.1
Internuclear distance/pm	74.14	74.14	(74.14)

<sup>(a)</sup>Data refer to H<sub>2</sub> of normal isotopic composition (i.e. containing 0.0156 atom % of deuterium, predominantly as HD). All data refer to the mixture of *ortho*- and *para*-forms that are in equilibrium at room temperature.

<sup>(b)</sup>1 atm = 101.325 kN m<sup>-2</sup> = 101.325 kPa.

For example, the mp of T<sub>2</sub> is above the bp of H<sub>2</sub>. Other forms such as HD and DT tend to have properties intermediate between those of their components. Thus HD has mp 16.60 K, bp 22.13 K,  $\Delta H_{\text{fus}}$  0.159 kJ mol<sup>-1</sup>,  $\Delta H_{\text{vap}}$  1.075 kJ mol<sup>-1</sup>,  $T_c$  35.91 K,  $P_c$  14.64 atm and  $\Delta H_{\text{dissoc}}$  439.3 kJ mol<sup>-1</sup>. The critical temperature  $T_c$  is the temperature above which a gas cannot be liquefied simply by application of pressure, and the critical pressure  $P_c$  is the pressure required for liquefaction at this point.

Table 3.2 also indicates that the heat of dissociation of the hydrogen molecule is extremely high, the H–H bond energy being larger than for almost all other single bonds. This contributes to the relative unreactivity of hydrogen at room temperature. Significant thermal decomposition into hydrogen atoms occurs only above 2000 K: the percentage of atomic H is 0.081 at this temperature, and this rises to 7.85% at 3000 K and 95.5% at 5000 K. Atomic hydrogen can, however, be conveniently prepared in low-pressure glow discharges, and the study of its reactions forms an important branch of chemical gas kinetics. The high heat of recombination of hydrogen atoms finds application in the atomic hydrogen torch — dihydrogen is dissociated in an arc and the atoms then recombine on the surface of a metal, generating temperatures in the region of 4000 K which can be used to weld very high melting metals such as tantalum and tungsten.

### 3.2.2 Ortho- and para-hydrogen

All homonuclear diatomic molecules having nuclides with non-zero spin are expected to show nuclear spin isomers. The effect was first detected in dihydrogen where it is particularly noticeable, and it has also been established for D<sub>2</sub>, T<sub>2</sub>, <sup>14</sup>N<sub>2</sub>, <sup>15</sup>N<sub>2</sub>, <sup>17</sup>O<sub>2</sub>, etc. When the two nuclear spins are parallel (*ortho*-hydrogen) the resultant nuclear spin quantum number is 1 (i.e.  $\frac{1}{2} + \frac{1}{2}$ ) and the state is threefold degenerate ( $2S + 1$ ). When the two proton spins are antiparallel, however, the resultant nuclear spin is zero and the state is non-degenerate. Conversion between the two states involves a forbidden triplet–singlet transition and is normally slow unless catalysed by interaction with solids or paramagnetic species which either break the H–H bond, weaken it, or allow magnetic perturbations. Typical catalysts are Pd, Pt, active Fe<sub>2</sub>O<sub>3</sub> and NO. *Para*-hydrogen (spins antiparallel) has the lower energy and this state is favoured at low temperatures. Above 0 K (100% *para*) the equilibrium concentration of *ortho*-hydrogen gradually increases until, above room temperature, the statistically weighted proportion of 3 *ortho*:1 *para* is obtained, i.e. 25% *para*. Typical equilibrium concentrations of *para*-hydrogen are 99.8% at 20 K, 65.4% at 60 K, 38.5% at 100 K, 25.7% at 210 K, and 25.1% at 273 K (Fig. 3.1). It follows that, whereas essentially pure *para*-hydrogen can be obtained, it is never possible to obtain a sample

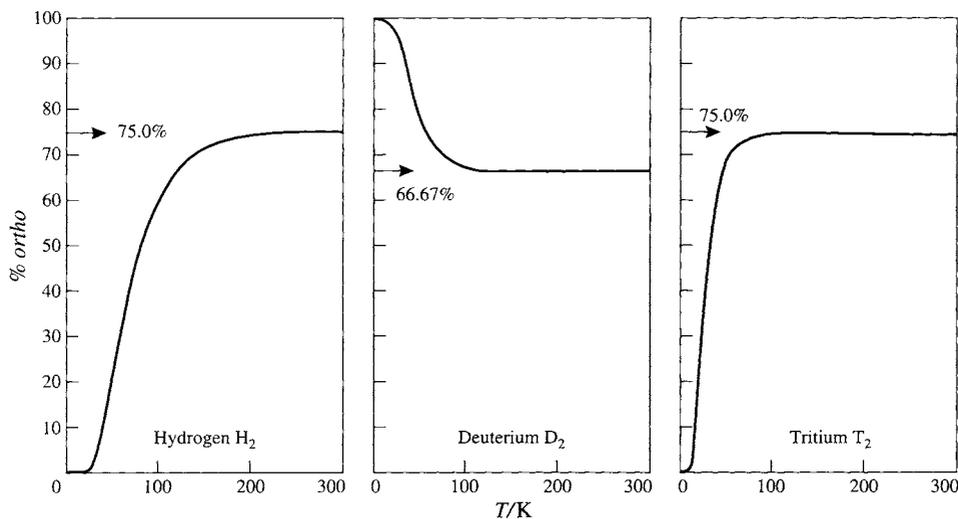


Figure 3.1 *Ortho-para* equilibria for  $H_2$ ,  $D_2$  and  $T_2$ .

containing more than 75% of *ortho*-hydrogen. Experimentally, the presence of both *o*- $H_2$  and *p*- $H_2$  is seen as an alternation in the intensities of successive rotational lines in the fine structure of the electronic band spectrum of  $H_2$ . It also explains the curious temperature dependence of the heat capacity of hydrogen gas.

Similar principles apply to *ortho*- and *para*-deuterium except that, as the nuclear spin quantum number of the deuteron is 1 rather than  $\frac{1}{2}$  as for the proton, the system is described by Bose–Einstein statistics rather than the more familiar Fermi–Dirac statistics. For this reason, the stable low-temperature form is *ortho*-deuterium and at high temperatures the statistical weights are 6 *ortho*:3 *para* leading to an upper equilibrium concentration of 33.3% *para*-deuterium above about 190 K as shown in Fig. 3.1. Tritium (spin  $\frac{1}{2}$ ) resembles  $H_2$  rather than  $D_2$ .

Most physical properties are but little affected by nuclear-spin isomerism though the thermal conductivity of *p*- $H_2$  is more than 50% greater than that of *o*- $H_2$ , and this forms a ready means of analysing mixtures. The mp of *p*- $H_2$  (containing only 0.21% *o*- $H_2$ ) is 0.15 K below that of “normal” hydrogen (containing 75% *o*- $H_2$ ), and by extrapolation the mp of (unobtainable) pure

*o*- $H_2$  is calculated to be 0.24 K above that of *p*- $H_2$ . Similar differences are found for the bps which occur at the following temperatures: normal- $H_2$  20.39 K, *o*- $H_2$  20.45 K. For deuterium the converse relation holds, *o*- $D_2$  melting some 0.03 K below “normal”- $D_2$  (66.7% *ortho*) and boiling some 0.04 K below. The effects for other elements are even smaller.

### 3.2.3 Ionized forms of hydrogen

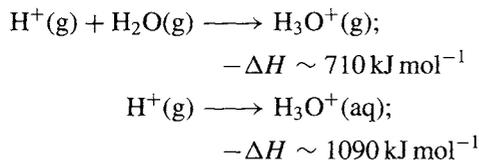
This section briefly considers the proton  $H^+$ , the hydride ion  $H^-$ , the hydrogen molecule ion  $H_2^+$ , the triatomic 2-electron species  $H_3^+$  and the recently established cluster species  $H_n^+$ ,<sup>(3,4)</sup>

The hydrogen atom has a high ionization energy ( $1312 \text{ kJ mol}^{-1}$ ) and in this it resembles the halogens rather than the alkali metals. Removal of the 1s electron leaves a bare proton which, having a radius of only about  $1.5 \times 10^{-3} \text{ pm}$ , is not a stable chemical entity in the condensed phase. However, when bonded to other species it is well known in solution and in

<sup>3</sup> N. J. KIRCHNER and M. T. BOWERS, *J. Chem. Phys.* **86**, 1301–10 (1987).

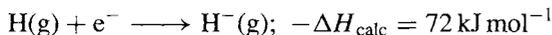
<sup>4</sup> M. OKUMURA, L. I. YEH and Y. T. LEE, *J. Chem. Phys.* **88**, 79–91 (1988), and references cited therein.

solids, e.g.  $\text{H}_3\text{O}^+$ ,  $\text{NH}_4^+$ , etc. The proton affinity of water and the enthalpy of solution of  $\text{H}^+$  in water have been estimated by several authors and typical values that are currently accepted are:



It follows that the heat of solution of the oxonium ion in water is  $\sim 380 \text{ kJ mol}^{-1}$ , intermediate between the values calculated for  $\text{Na}^+$  ( $405 \text{ kJ mol}^{-1}$ ) and  $\text{K}^+$  ( $325 \text{ kJ mol}^{-1}$ ). Reactions involving proton transfer will be considered in more detail in Section 3.5.

The hydrogen atom, like the alkali metals ( $ns^1$ ) and halogens ( $ns^2np^5$ ), has an affinity for the electron and heat is evolved in the following process:



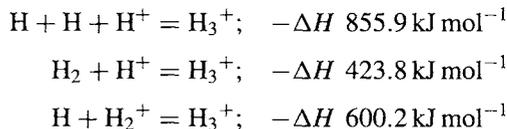
This is larger than the corresponding value for Li ( $57 \text{ kJ mol}^{-1}$ ) but substantially smaller than the value for F ( $333 \text{ kJ mol}^{-1}$ ). The hydride ion  $\text{H}^-$  has the same electron configuration as helium but is much less stable because the single positive charge on the proton must now control the 2 electrons. The hydride ion is thus readily deformable and this constitutes a characteristic feature of its structural chemistry (see p. 66).

The species  $\text{H}_2^+$  and  $\text{H}_3^+$  are important as model systems for chemical bonding theory. The hydrogen molecule ion  $\text{H}_2^+$  comprises 2 protons and 1 electron and is extremely unstable even in a low-pressure gas discharge system; the energy of dissociation and the internuclear distance (with the corresponding values for  $\text{H}_2$  in parentheses) are:

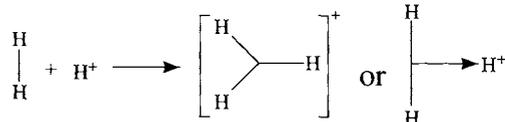
$$\begin{aligned} \Delta H_{\text{dissoc}} &255(436) \text{ kJ mol}^{-1}; \\ r(\text{H}-\text{H}) &106(74.2) \text{ pm} \end{aligned}$$

The triatomic hydrogen molecule ion  $\text{H}_3^+$  was first detected by J. J. Thomson in gas discharges and later fully characterized by mass spectrometry; its relative atomic mass, 3.0235, clearly distinguishes it from HD (3.0219) and from tritium

(3.0160). The “observed” equilateral triangular 3-centre, 2-electron structure is more stable than the hypothetical linear structure, and the comparative stability of the species is shown by the following gas-phase enthalpies:



The  $\text{H}_3^+$  ion is the simplest possible example of a three-centre two-electron bond (see discussion of bonding in boranes on p. 157) and is also a model for the dihapto bonding mode of the ligand  $\eta^2\text{-H}_2$  (pp. 44–7):



A series of ions  $\text{H}_n^+$  with  $n$ -odd up to 15 and  $n$ -even up to 10 have recently been observed mass-spectrometrically and characterized for the first time.<sup>(3,4)</sup> The odd-numbered species are much more stable than the even-numbered members, as shown in the subjoined table which gives the relative intensities,  $I$ , as a function of  $n$  (in  $\text{H}_n^+$ ) obtained in a particular experiment with a high-pressure ion source, relative to  $\text{H}_3^+$ .<sup>(3)</sup>

$n$	1	2	3	4	5	6
$10^4 I$	160	50	<b>10 000</b>	4.2	4200	210
$n$	7	8	9	10	11	
$10^4 I$	3200	7.4	2600	18	34	

The structures of  $\text{H}_5^+$ ,  $\text{H}_7^+$  and  $\text{H}_9^+$  are related to that of  $\text{H}_3^+$  with  $\text{H}_2$  molecules added perpendicularly at the corners, whereas those of  $\text{H}_4^+$ ,  $\text{H}_6^+$  and  $\text{H}_8^+$  feature an added H atom at the first corner. Typical structures are shown below. The structures of higher members of the series, with  $n \geq 10$  are unknown but may involve further loosely bonded  $\text{H}_2$  molecules above and below the  $\text{H}_3^+$  plane. Enthalpies of dissociation are  $\Delta H_{300}^\circ (\text{H}_5^+ \rightleftharpoons \text{H}_3^+ + \text{H}_2)$   $28 \text{ kJ mol}^{-1}$  and  $\Delta H_{300}^\circ (\text{H}_7^+ \rightleftharpoons \text{H}_5^+ + \text{H}_2)$   $13 \text{ kJ mol}^{-1}$ .<sup>(4)</sup>