1

Introduction to Basic Properties of Hydrogen

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1.1 BASICS ABOUT THE HYDROGEN ELEMENT

Hydrogen is known as the most abundant element in the universe. It accounts for about 75% of the known mass of the universe. Hydrogen is a major element in many known stars and planets. For example, stars, when formed in the present Milky Way galaxy, are composed of about 71% hydrogen and 27% helium, as measured by mass, with a small fraction of heavier elements [1]. Stars spend about 90% of their lifetime fusing hydrogen to produce helium in high temperature and high pressure reactions near the core. Thus, hydrogen is a critical element for the very existence of the universe.

Both the hydrogen atom (H) and hydrogen molecule (H_2) have many unique chemical and physical properties. Hydrogen is also a major component of many important molecules, such as water, hydrocarbons, proteins, and DNA. It is safe to say that there would be no life if there were no hydrogen.

The atomic hydrogen is the smallest and lightest element. The hydrogen atom consists of one proton (H^+) and one electron, with no neutrons, and is usually denoted as ^1H or just H (also named as protium sometimes). Hydrogen has two common isotopes, deuterium (D or ^2H) and tritium (T or ^3H), that contain one and two neutrons, respectively, in addition to the one proton

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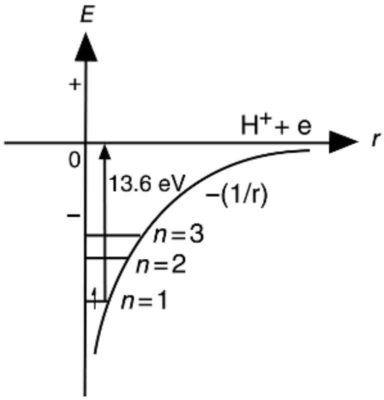

FIGURE 1.1 Relevant energy level of the ground electronic state of the H atom and its ionized state ($H^+ + e$). *E* is energy, *n* is the principal quantum number, *r* is the distance between the electron and proton; $-(1/r)$ is the Coulombic attraction between the electron and proton; and 13.6 eV corresponds to the ionization energy of the H atom from its ground electronic state ($n = 1$ or 1s atomic orbital).

and electron that H contains. The abundance is 99.895%, 0.015%, and trace amount, respectively, for H, D, and T. While the mass differs significantly among the three isotopes, their electronic structures and properties are very similar since the neutrons have essentially no effect on the electronic properties that are mainly determined by the electron and proton. Other highly unstable nuclei (^{4}H to ^{7}H) have been synthesized in the laboratory but not observed in nature.

The ionization energy for H atom is 13.6 eV or 1312.0 kJ mol^{-1}, equivalent to a photon energy of 92 nm. Thus, H atom is highly stable under normal conditions. The ionized form of the H atom is the proton, H^+, which has many interesting and unique properties of its own. It is the lightest and smallest atomic ion. Figure 1.1 shows the relevant energy levels for the ground electronic state of H atom relative to its ionized state ($H^+ + e$). In water, the proton is in the form of H_3O^+ and plays a critical role in many biological processes. The proton is also related to acids and bases, which are two essential classes of compounds in chemistry and important for chemical industry.

Hydrogen atoms are reactive and can be combined with many elements to form a huge number of different compounds, including most organic and biological compounds, such as hydrocarbons, polymers, proteins, and DNA. For most organic compounds, the hydrogen is bound to the atoms of carbon and, to a lesser degree, nitrogen, oxygen, or other atoms, such as phosphorus and sulfur. The H atom only forms a relatively strong single bond with these atoms.

1.2 BASICS ABOUT THE HYDROGEN MOLECULE

When two hydrogen atoms combine, they form a stable molecule, H_2, with a single and strong covalent bond. The equilibrium bond length is 0.74 Å. The bond dissociation energy is 4.52 eV or 436 kJ mol^{-1}.

Extensive experimental and theoretical studies have been done on H_2 in terms of its electronic structures, optical properties, magnetic properties, and reactivity with other elements or compounds. Its small size and light mass make it convenient for theoretical and computational studies. For example, potential energy surfaces (PES) or curves for many electronic states of H_2 have been calculated with high accuracy [2, 3]. Figure 1.2 shows some examples of PES of low-lying electronic states of H_2 [4, 5]. The ground electronic state and the first few excited states are all bound with respect to the bond distance between the two hydrogen atoms.

Because the large energy difference between the ground and first excited electronic states of H_2 (near 12 eV), there is no absorption of visible or UV light by H_2, thus H_2 gas is colorless. H_2 does absorb light in the vacuum UV (VUV) region of the spectrum. Since the three lowest excited electronic states are all bound, they are expected to be relatively long-lived and lead to fluorescence when excited by light in the VUV region.

Molecular hydrogen has interesting magnetic properties, mainly due to its nuclear spin properties. There are two different spin isomers of H_2, ortho and

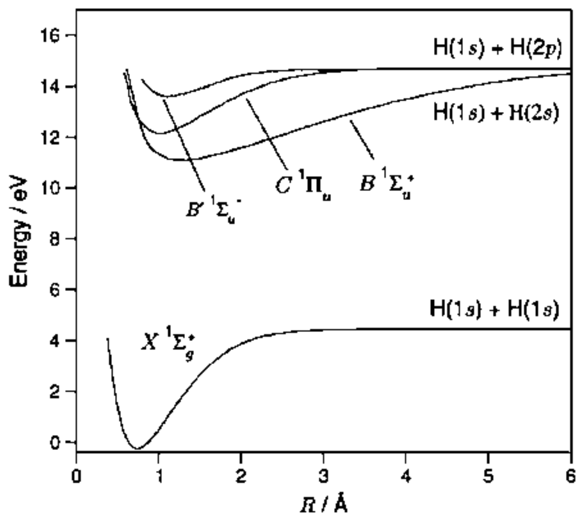

FIGURE 1.2 Examples of several low-lying PES of H_2. *Source*: Reproduced with permission from Flemming et al. [4].

para, which differ by the relative spin of their nuclei. In the orthohydrogen form, the spins of the two protons are parallel to each other and form a triplet state with a molecular spin quantum number of 1 ([1/2] + [1/2]). In the parahydrogen form, the proton spins are antiparallel to each other and form a singlet state with a molecular spin quantum number of 0 ([1/2] − [1/2]). At standard temperature and pressure, H_2 gas contains about 75% of the ortho form and 25% of the para form, known as the normal form. The ortho form has a higher energy than the para form, and is thus unstable and cannot be purified. The ortho/para ratio depends on temperature, and decreases with decreasing temperature. This ratio in condensed H_2 is an important consideration in the preparation and storage of liquid hydrogen (see Chapter 5), since the conversion from ortho to para is exothermic and produces enough heat to evaporate some of the hydrogen liquid, leading to loss of liquefied material. The interconversion between the two forms and hydrogen cooling are often facilitated by catalysts such as ferric oxide, activated carbon, or some nickel compounds.

H_2 is a stable molecule but can react with a number of elements and molecules under certain conditions. One classic example is reaction with oxygen (O_2) to form water. Such a reaction can be carried out by way of combustion, which is fast and violent, as will be discussed in more detail in Chapter 8.

Among the many interesting properties of H_2, its potential use as a clean and renewable fuel has attractive considerable attention, especially given the increasing demand of energy and adverse environmental impact associated with use of fossil fuel. H_2 is an ideal fuel in several ways, including clean byproduct, water, in energy production process and abundance, making it potentially low cost. For example, Chapter 3 covers recent research efforts on photoelectrochemical water splitting for hydrogen generation. However, there are currently some major obstacles toward the practical use of hydrogen as a fuel, including hydrogen generation, storage, transport, and utilization. Efficiency and cost are two important factors to consider for each of these aspects. Safety is another factor of concern.

A molecular ion, H_3^+, has been found in interstellar medium (ISM), which is generated by ionization of H_2 from cosmic rays. It is one of the most stable ions in the universe. The neutral form, H_3, is not stable and can only exist in an excited state for a short period of time.

1.3 OTHER FUNDAMENTAL ASPECTS OF HYDROGEN

Besides forming the hydrogen molecule, H_2, the hydrogen element is involved in the formation of a large number of compounds, including water, hydrocarbons, and many important biological molecules, such as proteins and

DNAs. Water is essential for life, and the water molecule contains two hydrogen atoms and one oxygen atom, bound together in a bent geometry. The H–O–H bond angle is 104.5° in the ground electronic state. The bent geometry results in a net permanent dipole moment of the water molecule. Hydrogen bonding between water molecules is another unique feature of water. The combination of hydrogen bonding and permanent dipole moment are largely responsible for the fact that water is a liquid at room temperature and 1 atm, a property critical for life. If we count the two lone pairs of electrons, water molecule has a near tetrahedral geometry with the oxygen atom in the center. In its ground electronic state, the water molecule has three vibrational frequencies: symmetric stretch (3657 cm^{-1}), antisymmetric stretch (3756 cm^{-1}), and bending (1595 cm^{-1}), based on gas phase data. The relatively high vibrational frequencies, in conjunction with fast rotation, are important for its role as a common solvent and other significant properties, such as heat conduction.

Most organic molecules contain hydrogen atoms. Examples include saturated and unsaturated hydrocarbons, aromatic compounds, lipids, alcohols, ethers, and esters. Many small drug molecules, polymers, and petrochemicals, such as gasoline, are examples of important molecules that contain hydrogen.

Almost all biological molecules contain hydrogen, for example, proteins and DNAs. Of course, complex structures, such as cells, viruses, bacteria, and tissues, all contain hydrogen as an essential element in their constituent components.

1.4 SAFETY AND PRECAUTIONS ABOUT HYDROGEN

Hydrogen poses several safety concerns, from potential detonation and fire in air to being an asphyxiant in its pure, oxygen-free form. For instance, as a cryogen, liquid hydrogen presents dangers associated with very cold liquids. Hydrogen “dissolved” in metals can lead to cracks and explosions. Hydrogen gas in air may spontaneously ignite, and the detonation parameters, for example, critical detonation pressure and temperature, strongly depend on the container geometry. Thus, hydrogen must be handled with extreme care and caution in gaseous or liquid form.

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