

2 Liquid Water

2.1 Some Facts and Anomalies

Water seems at first sight to be a very simple molecule and indeed, few molecules are smaller. Its size, however, belies the complexity of its properties, and these properties seem to fit ideally into the requirements for carbon-based life as no other molecule can do. Organisms consist mostly of liquid water, which performs many functions and should never be considered simply as an inert diluent. But, in spite of much work, many of the water properties are puzzling. It has often been stated that life depends on the anomalous properties of water. For instance, it takes a relatively large amount of heat to raise water temperature by one degree. This enables the world's oceans to store enormous amounts of heat, producing a moderating effect on the world's climate, and it makes it more difficult for marine organisms to destabilize the temperature of the ocean environment even as their metabolism produces copious amounts of waste heat. In addition, liquid water expands when cooled below 4°C. This is unlike most liquids, which expand only when heated. This explains how ice can sculpt geological features over millions of years through the process of erosion. It also makes ice less dense than liquid water, and enables ice to float on top of the liquid. This property allows ponds to freeze on the top and has offered a hospitable underwater location for many life forms to develop on this planet.

Most biochemical and industrial processes occur in solution, making it crucial to be able to understand the participation of the solvent, specifically, solvation effects, in determining chemical reactivity. Water is an excellent solvent due to its polarity, small size and high dielectric constant, particularly for polar and ionic compounds and salts. Its solvation properties are so impressive that it is difficult to obtain really pure water. Water ionizes and allows easy proton exchange between molecules, thus contributing to the richness of the ionic interactions in biology. The unique hydration properties of water towards biological macromolecules (particularly proteins and nucleic acids) to a large extent determine their

three-dimensional structures, and hence their functions, in solution [5].

Its striking number of unusual properties may be largely ascribed to its ability to hydrogen-bond (H-bond). Yet, bulk water and solvate water (both cation and anion solvation) is not well understood in terms of the microscopic properties of its constituent water molecules and their mutual interaction.

2.2 Geometric and Electronic Structure

The isolated water molecule, H_2O , has a simple molecular structure. It is composed of one oxygen atom and two hydrogen atoms. Each hydrogen atom is covalently bound to the oxygen via a shared pair of electrons, see Fig. 2.1a.

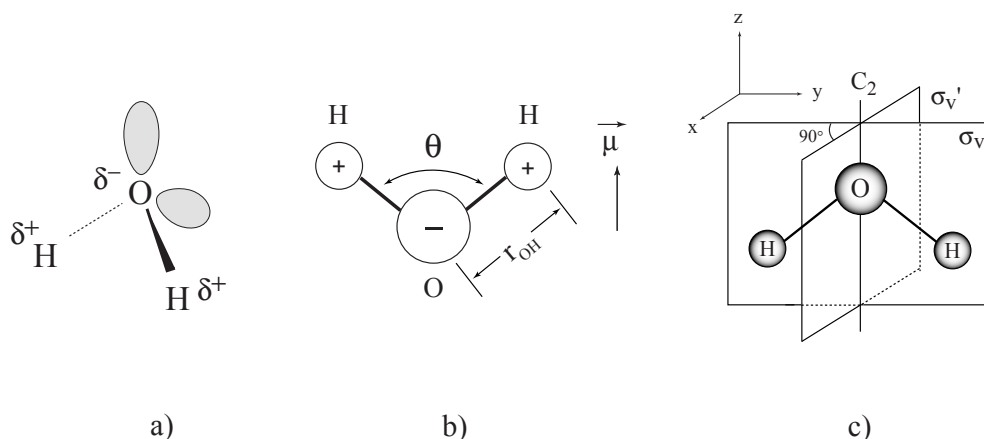


Figure 2.1: a) The water molecule; gray ovals depict the lone pair orbitals. b) Dipole moment of the water molecule. c) Symmetry of the water molecule.

In the ground state the molecular orbital (MO) configuration of water is [6]

$$(1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (1b_1)^2,$$

where $1a_1$ corresponds to an O $1s$ orbital. The lowest unoccupied MOs are $4a_1$ and $2b_2$ σ antibonding orbitals. In this work the three outermost occupied orbitals are referred to as the outer valence band while the $2a_1$ to as the inner valence band (see Fig. 2.2). The $2a_1$ is strongly O $2s$ - H $1s$ bonding and has largely O $2s$ character. The $1b_2$ and $3a_1$ states arise from bonding interactions between O and H with the former having pure bonding character consisting of a linear combination of O $2p_y$ and H $1s$ orbitals. The latter predominantly consists of a linear combination of O $2p_z$ and H $1s$ orbitals, having both bonding and non-bonding character. The $3a_1$ state possesses the symmetry of the molecule, whereas the

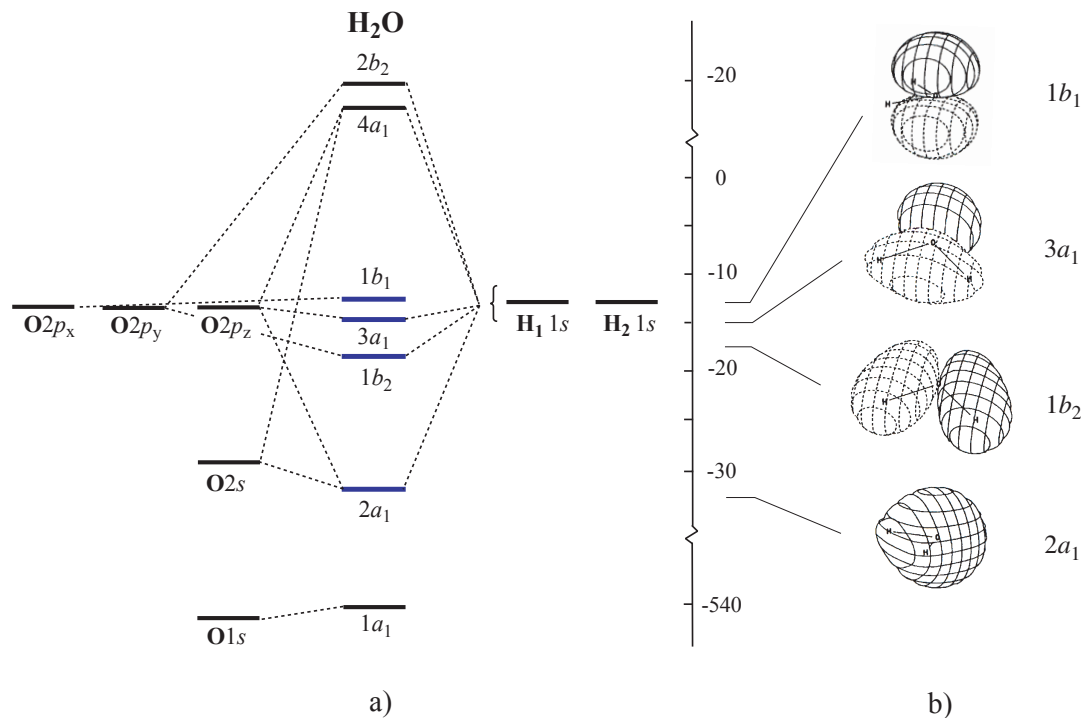


Figure 2.2: a) Molecular orbital energy level diagram of H₂O [6]. b) Delocalized molecular orbitals of water [7].

$1b_1$ and $1b_2$ states are asymmetric about the mirror planes in and normal to the molecular plane, respectively [7] (see below). The $1b_1$ state is comprised primarily of oxygen lone pair character (O $2p_x$) and it is thus non-bonding.

Due to the two unshared oxygen lone pair electrons (gray clouds in Fig. 2.1a) the water molecule has a partial negative charge near the oxygen atom and a partial positive charge near the hydrogen atoms. This uneven distribution of the electron density makes the water molecule polar, giving rise to a dipole moment, $\mu = 1.854 \text{ D}^1$ [8], with the orientation as indicated in Fig. 2.1b. The direction is consistent with detailed calculations of charge distribution for H₂O which reveal high electron density around the oxygen atom.

Typically, the water molecule is described as having four, approximately tetrahedrally arranged sp^3 -hybridized electron pairs [6], two of which are associated with hydrogen atoms. In a perfect tetrahedral configuration, with the oxygen in the center and the hydrogens and the lone pairs in the corners, the bond angles would all be 109.47° . This kind of bonding pattern is indeed found in condensed phase such as hexagonal ice. In free water the strongly negative lone pair gives rise to a considerable repulsion, which in turn acts to push the

¹ 1 Debye = $3.3356 \times 10^{-30} \text{ C}\cdot\text{m}$

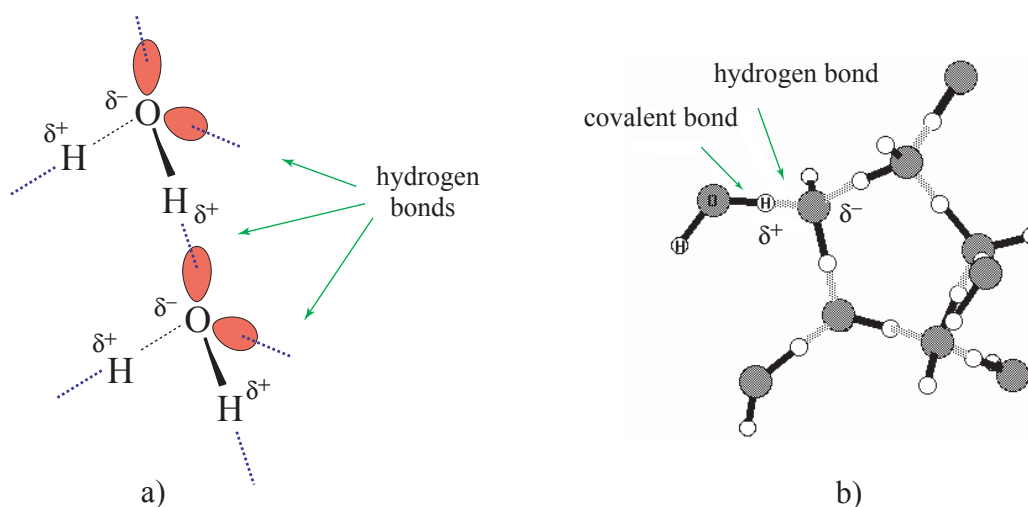


Figure 2.3: Illustration of the H-bonding in liquid water. a) Showing the role of the lone pair electrons (gray ovals). b) H-bonding shown for 10 water molecules.

hydrogen atoms closer together. This results in the water bond angle of 104.45° (see Θ in Fig. 2.1b).

The water molecule has two mirror planes of symmetry and a two-fold rotation axis (C_{2v} symmetry, see Fig. 2.1c). The hydrogen atoms may possess parallel (ortho-water) or antiparallel (para-water) nuclear spin, which are randomly oriented in the absence of a magnetic field. By applying an external magnetic field, the nuclear spins orient themselves in the direction of the field, or opposite to it, which gives rise to unequal energy. The nuclei in the lower spin state can be excited into the upper spin state. This transition provides the basis for the nuclear magnetic resonance (NMR) spectroscopy.

Water molecules in the liquid and solid phases exhibit two types of O-H interactions: strong covalent O-H-bonds (bond length $r_{\text{OH}} = 0.957 \text{ \AA}$) *within* the water molecules and relatively weak bonds *between* the molecules. The weak electrostatic attraction between the partial positive and the partial negative ends of the water molecules allows for the formation of a highly organized *inter-molecular* network, the hydrogen bonding (H-bonding) in liquid water.

Hydrogen bonds have about a tenth of the strength of an average OH covalent bond, and are being constantly broken and reformed in liquid water (on a picosecond time scale). The structure of a H-bonding network of liquid water is presented in Fig. 2.3a,b. Fig. 2.3a depicts the attraction of the δ^+ hydrogen atom to the δ^- oxygen lone pair. Notice that each water molecule can potentially form four hydrogen bonds with surrounding water molecules, see

Fig. 2.3b. Recent experimental (vibrational spectroscopy, neutron and X-ray diffraction) and theoretical (molecular dynamics) studies have revealed, however, that liquid water contains a fraction of water molecules with broken H-bonds [9]. H-bonding, despite being weak, holds the key to water's peculiar behavior. For instance, it is responsible for the large cohesive energy and the latent heat, the high boiling point, the high surface tension, and the reluctance to dissolve hydrophobic solutes. On the other hand water strongly binds to and dissolves polar (e.g. salts) and hydrophilic compounds.

2.3 Aqueous Solutions and Solvation

Ion solvation in the liquid phase is a process crucial to almost any scientific and also technological discipline. Water, in particular, is the most important solvent in nature, ranging from biological systems to seawater, the latter having an enormous impact on the world climate. There are various forms of solvation, even for water, and there is a naturally high demand for understanding the underlying mechanisms. Generally, one distinguishes ions' solvation by their ability to either make or break the bulk water structure². One special case of a water structure maker, namely the hydrophobic tetrabutylammoniumiodide, will be discussed in 4.3. E.g. non-electrolytes, such as sugar, contain a substantial number of hydroxyl groups that serve as H-donors for water molecules, which orient themselves along the dipole moments of these polar side groups [10]. Thus, a specific molecular structure is created by the solvent. Also, the net size increase of a solute by its hydration shell may affect the enzymatic activity in biological systems. Successful molecular design or peptide engineering will necessarily include an assessment of solvation for conformational stability [11]. Water ionizes and allows for easy proton exchange between molecules, so contributing to the richness of the ionic interactions not only in biology [5]. Besides, numerous phenomena in chemical physics can only be studied in liquids and also technologically relevant processes take place in the presence of water. The vast majority of molecular interactions in living systems occur in an aqueous environment and also geological structures are constantly exposed to water. Thus, in order to understand solvation phenomena in nature, one would need to study processes

²*Structure making* refers to the enhanced structure (primarily within the solvation shell) relative to bulk water. At larger distance (outer shells) the water molecules may be less ordered than in bulk water, and this is thought of as a consequence of *structure breaking*. Ions are referred to as *structure makers* (kosmotropes) or *structure breakers* (chaotropes) according to their net effect on the bulk water, which is inherently related to the system's entropy change.

taking place particularly in liquid water. Again, this information may be well accessed by photoelectron spectroscopy.

Solvation processes are driven by the ion-ion and ion-solvent interactions, which in turn are controlled by the respective interaction potentials. In addition, specific structural effects, such as hydrogen bonding, must be taken into account. A major issue is the distance over which the ion-solvent interaction extends into the bulk solution. Primary and secondary (or even more) solvation shells around the ions are chosen as the bases for various models, and solvated clusters in the gas phase are considered invaluable model systems for bulk liquid solvation (see also section 4.2.5).

The first theoretical concept to treat single ion solvation was the Born model [12]

$$\Delta G^{Born} = -\frac{Z^2 e^2}{8\pi\epsilon_0 R} \left(1 - \frac{1}{\epsilon}\right), \quad (2.1)$$

which expresses the Gibbs energy of solvation of an ion of radius R and charge Ze in a solvent of relative permittivity ϵ , as the difference of ion self-energies³, in the dielectric medium and in vacuum [10]. Dielectric continuum models, like the Born model and its extensions taking into account local permittivity around the ions [13] or introducing effective ionic radii [14,15], consider the solvent as a shielding medium without any structure. More advanced theory which takes into consideration the structure of polar solvents, generally suffers from the assignment of exact interaction potentials. A discussion of the elementary solution processes can be found in Ref. [10].

The spontaneous solvation (hydration) of salts in water shows that the interaction between the solvent and the solute is stronger than that of both, solvent-solvent and solute-solute. The free energy of hydration associated with the energies of interaction between solvent and solute molecules is about 200 to 400 kJ/mol (2 to 4.5 eV). To understand the properties of salts in water, one has to consider the electrostatic interactions of positively and negatively charged molecules, cations and anions, respectively, with the molecular dipole of water molecules. A salt is a pair of ions, of opposite but equal charge, which interacts forming salt pairs having no net charge, yet a dipole moment.

In the salt crystal, strong coulombic forces initially draw ions close together before short-range repulsive forces come into play and an equilibrium interionic distance is established. The result is that a large amount of energy is needed to break down the lattice. If a NaCl

³This is the free energy, which results from the ion's interaction with its surrounding. This quantity may be determined via a charging process by which the charge of a given ion is increased from zero to Ze . This yields $U_{i\text{self}} = Z^2 e^2 / 8\pi\epsilon_0 R$ [10].

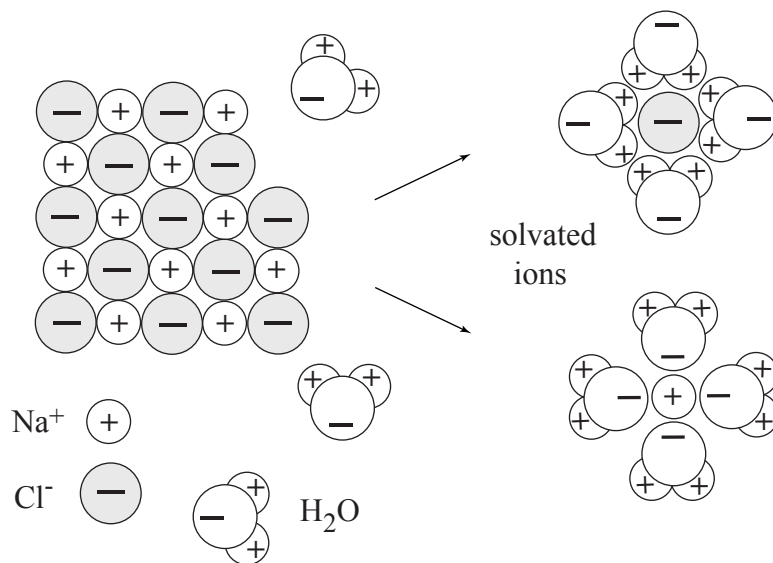


Figure 2.4: Cartoon depicting a NaCl crystal dissolving in water (left) and subsequent ion solvation (right).

crystal is introduced into a solvent such as water, the attractive forces between the ions will be considerably reduced due to high relative permittivity of water. As a result the ionic attraction between Na⁺ and Cl⁻ becomes much weaker and NaCl will readily dissolve in water to produce freely moving Na⁺ and Cl⁻ ions. However, the reduction of the attractive energy in the aqueous phase would not be sufficient to dissolve NaCl. The decisive role is played by the strong dipole moment of water which preferentially orients its negative pole towards a cation and its positive pole towards an anion. The resulting layer of the water molecules is called the solvation shell of the ion and the energy gained in the solvation process usually tips the balance in favor of dissociation [16]. For an illustration, Fig. 2.4 is a cartoon depicting a NaCl crystal dissolving in water, as well as the solvation of the anion and cation. Fig. 2.5 is another schematic showing a more realistic picture of how solvated ions, Na⁺ and Cl⁻, are embedded in the water hydrogen bonding network. Water molecules bind to the Cl⁻ anion via hydrogen bonds. This imposes considerable disturbance on the native bulk water structure as compared to solvation of positive ions [2], in which case the oxygen faces the ion.

Experiments show that water is ordered by small or multivalent ions and disordered by large monovalent ions (compare footnote 2). Clearly, changes of the water structure by ions also implies a change of the properties of water; likewise are the ion properties affected by the solvating water molecules. Water ordering correlates with the ion's charge density. The

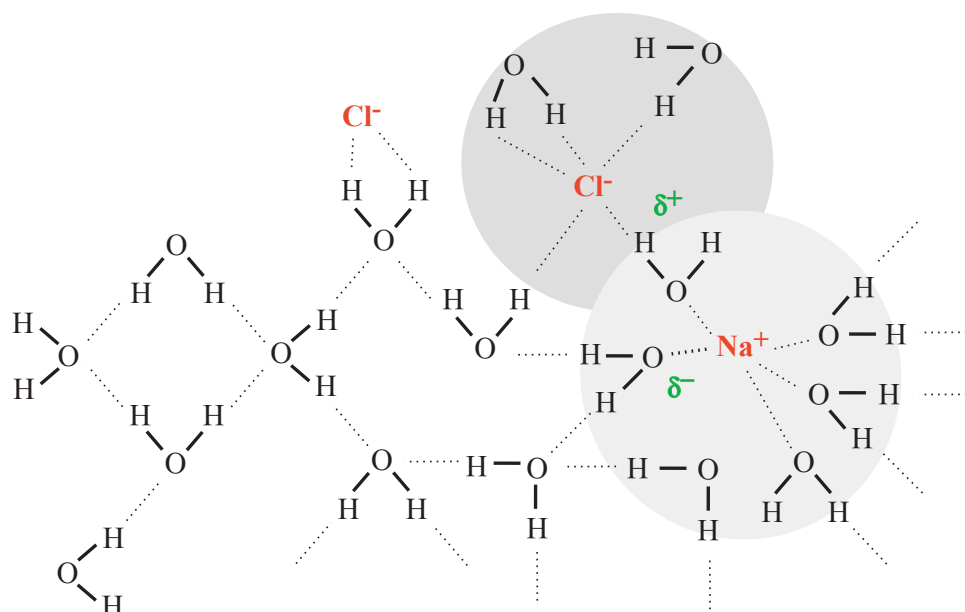
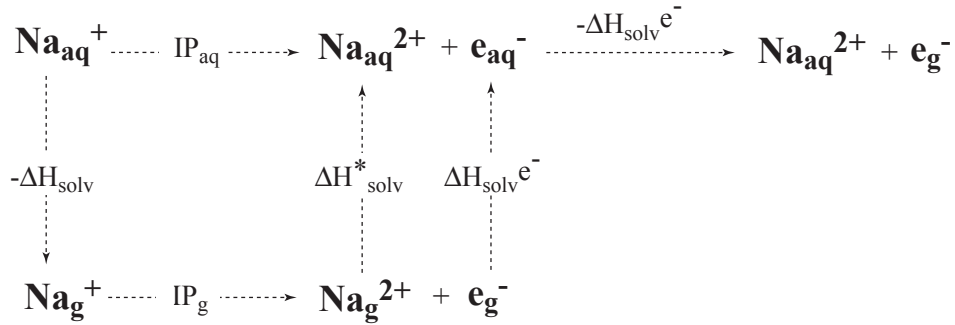


Figure 2.5: Schematic depicting the difference of anion and cation solvation. For anion solvation (here Cl^-) the hydrogen atoms are directed towards the ion, while for cation (here Na^+) water molecules are re-oriented with the oxygen atoms pointing towards the ion. The shaded circles roughly indicate the respective solvation shell.

smaller the ion, the stronger its charge density. This means more water molecules will be attracted to it and thus the smaller the ion the larger the solvation shell radius (and the slower mobility it has). Theoretical models [17] proposed that ion effects on water structure could be explained by a competition between ion-water interactions, which are dominated by charge density effects, and water-water interactions, which are dominated by hydrogen bonding. Based on this argument anions have a weaker effect in water ordering than cations. This is due to the asymmetry of charge in a water molecule: the negative end of water's dipole is closer to the center of the molecule than the positive end. Therefore, anions would see a larger electrostatic potential at the surface of the water molecule than cations.

Furthermore, increasing the cation size diminishes the electrostatic force of the ion on the water, leading to increased water-water hydrogen bonding, as would be seen around nonpolar solutes [17]. A similar trend occurs for anions: water structure around a small anion is controlled by an electrostatic mechanism, while the water structure around larger anions is controlled by hydrogen bonding. A notable difference between anions and cations is the ion size required to achieve a given level of water ordering. Larger anions have the same effect on water ordering as smaller cations.

From an experimental point of view the *single* ion solvation properties cannot be deter-



$$\text{BE}_{\text{aq}} = -\Delta H_{\text{solv}} + \text{IP}_{\text{g}} + \Delta H_{\text{solv}}^*$$

Figure 2.6: Simplified presentation of the photoionization process of a solvated cation by a Born-Haber cycle. ΔH_{solv} and ΔH_{solv}^* denote the respective solvation energy, and IP are the respective ionization potentials. IP_{aq} may be identified with BE_{aq} , the energy required to remove the outermost electron of solvated Na_{aq}^+ into vacuum.

mined as anion and cation contributions are indistinguishable. Moreover, various situations of interactions between solvated ions may occur in different systems. In some cases, ions may share solvation shells to some extent. This aspect will be further detailed in sections 4.2.6 and 4.3.

The remainder of this section discusses how the primary quantity measured in the present study, i.e. the electron binding energy of aqueous ions E_{aq} (which is a microscopic quantity), relates to the enthalpy of solvation, ΔH_{solv} , typically reported in text books. As mentioned above, salts have considerable lattice energies and thus a large amount of energy is required for dissolving them, i.e. forming solutions with cations and anions. ΔH_{solv} , of course, only accounts for one sub-process within the thermodynamic cycle for dissolution of a salt in water⁴ and it is the energy gained by formation of the solvation shell around the ion. The relation between E_{aq} and ΔH_{solv} may be reasonably well presented within a Born-Haber

⁴The energy of the total process (e.g. the free energy or enthalpy) is the sum of the effects of separating ions from the lattice and solvating the ions (compare Fig. 2.4). A given salt is soluble in water if the hydration energy of both the anions and cations exceeds the lattice energy. One may also have to account for entropy contributions, $\Delta G = \Delta H - T\Delta S$, associated with structural changes during the solvation process. On the one hand would the transfer of ions from the solid to the solution correlate with an increase of ΔS , on the other hand may the rearrangement of the solvent molecules lead to some considerable decrease of ΔS of the solvent. Often, the net entropy contribution is negligible, in which case $\Delta G = \Delta H$.

cycle as suggested in Fig. 2.6 for aqueous Na^+ .

Apparently, the energy of the entire process of *photoemission* from an aqueous ion can be approximated by the sum of three quantities, the solvation enthalpy of the initial ion as well as the ionized ion, and of the ionization energy of the gas-phase species. The unknown quantity in the scheme is the value for ΔH_{sol}^* , which is the energy gained by solvating the doubly charged alkali atom. In 4.2.5 it will be shown how to describe the photoionization process of solvated ions within the Born continuum model. It will be also shown, however, that any such a thermodynamic treatment, without assuming any structural details of the solvate complex, is not capable to describe microscopic processes which are important to understand solvation.