Chapter 1

Introduction

Gas phase studies of small molecules and clusters yield important information about the evolution of molecular properties with size in the absence of any interaction with the environment. In this size regime each atom counts, meaning that by adding or removing a single atom important changes in chemical and physical properties of molecular systems occur. Spectroscopic studies on small charged systems are convenient because the ions can be mass-selected and investigated under well defined conditions. Small systems have also the advantage that high level theoretical studies can be performed and together with the experiment characteristics of the molecules can be investigated and model systems can be proposed.

Infrared spectroscopy in combination with quantum chemical calculations is one of the most direct and general applicable approach for the investigation of the structures as well as other molecular properties. Experimental investigations of gas phase ions by infrared spectroscopy was hindered in the past by the lack of tunable and intense lasers which emit light in the region where most of the fundamental transitions occur, i. e., below 2000 cm^{-1}. High laser intensities are required in these experiments due to low ion densities. The development of free electron lasers enabled the measurement of infrared spectra of molecular systems in the gas phase in the region of interest. We combine for the first time an ion guiding tandem mass spectrometer with an intense, tunable infrared free electron laser in order to measure infrared spectra of gas phase ions with increased selectivity and sensitivity. In this thesis two types of systems were investigated, namely: a) strongly hydrogen bonded ions: protonated and deprotonated water ions and hydrogen dihalide anions, and b) vanadium oxide cations.

Strong Hydrogen Bonds in Protonated Water Clusters

The concept of hydrogen bond was first introduced by M. L. Huggins, W. M. Latimer and W. H. Rodebush.[1] L. Pauling defined the hydrogen bond in his book "The Nature of the Chemical Bond"[2] as follows: "Under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms instead of only one, so that it may be considered to be acting as a bond between them. This is called a hydrogen bond". Hydrogen bonds can be classified according to their strength into strong, moderate and weak hydrogen bonds. The strength of hydrogen bonds reaches from 2 $kcal/mol$ (0.09 eV) for organic molecules up to 25 $kcal/mol$ (1.08 eV) for HF complexes in neutral systems and 37 $kcal/mol$ (1.6 eV) for the $(FHF)^-$ anion which has one of the strongest known hydrogen bond.[3] Strong hydrogen bonds are characterized by a single-well potential, whereas the weak H-bonds represent a double well minimum as shown in Figure 1.1. The moderate strength hydrogen bonds have
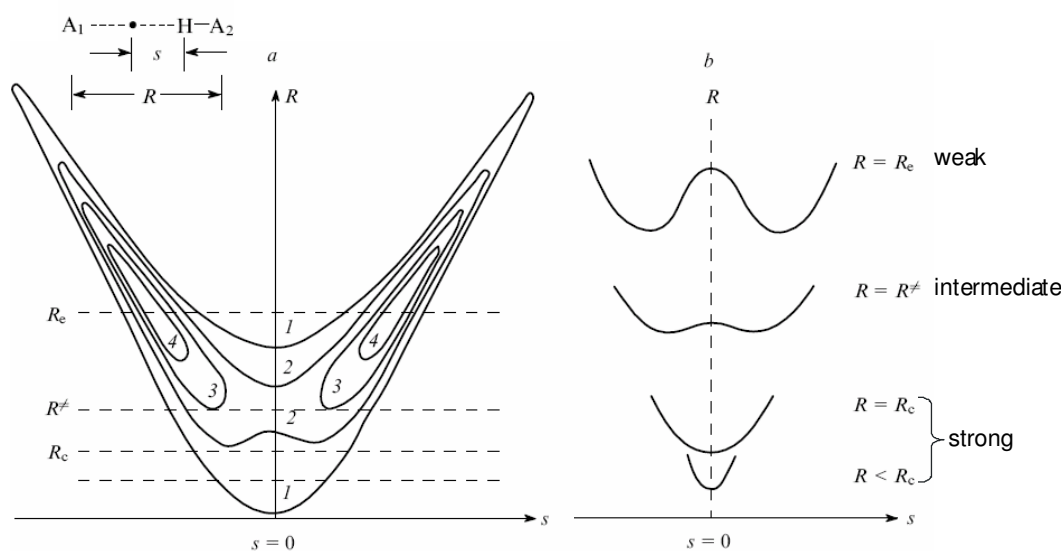

Figure 1.1: Typical symmetric potential energy surface for proton transfer reaction. a) General view of the potential energy surface. b) PES cross-sections along the coordinate s for different R values. The projections of the cross-sections on the R, s plane are shown by a dashed line in a). Adapted from Basilevsky and Vener.[4]

a rather low barrier between the two minima (see Figure 1.1), with the barrier height close (slightly above or below) to the zero point energy level.

Hydrogen bonds play an important role in chemistry and biology, governing diverse phenomena, e.g., the properties of water[5] such as the high proton mobility, high boiling temperature and the low density of ice. Hydrogen bonds determine the sec-
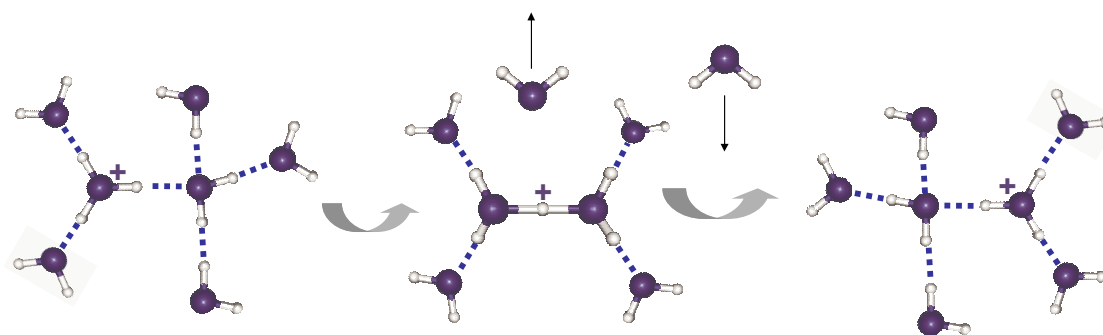
Figure 1.2: Schematics of the proton transfer in liquid water. (O in blue, H in white.)

ondary structure of proteins and DNA[6] and are involved in the mechanism of enzyme catalysis[3] as well.

The anomalously high mobility of protons in liquid water raised the interest of many scientists in understanding the underlying mechanism of the proton transfer process.[7–10] In a simplified picture, the proton transfer process can be explained by the Grotthuss mechanism[11] which involves proton "hops" between hydrogen bonded water molecules followed by a reorganization of the hydrogen-bonded network. Two structures have been proposed to be important in the proton transfer process in water. Eigen[12] proposed the formation of an $H_9O_4^+$ cation, in which an H_3O^+ core is solvated by three H_2O molecules. Zundel[13] proposed another structure, $H_5O_2^+$, in which the proton is shared equally by two water molecules. Using molecular dynamics simulations, Marx *et al.*[14] showed that the Eigen cation $H_9O_4^+$ as well as the Zundel cation $H_5O_2^+$ appear as limiting structure in the proton transfer process (see Figure 1.2).

The Zundel and Eigen cations $H_5O_2^+$ and $H_9O_4^+$ play an important role in proton pump processes in proteins such as the bacteriorhodopsin in which protons are pumped to the extracellular side of the membrane. The photoisomerization of the retinal chromophore induces a series of protonation stage changes, followed by the release of a proton to the extracellular side. X-ray crystallography as well as FTIR experimental studies[16] predict the existence of water molecules in the structure of the bacetriorhodopsin which function as proton release groups. Spassov *et al.*[17] and D. Marx[15] suggested that the proton is stored in form of protonated water clusters, possibly $H_5O_2^+$ as shown in Figure 1.3. Rousseau *et al.*[18] studied the structure and dynamics of protonated water networks on the extracellular side of the transmembrane proton pump bacteriorhodopsin. Their calculations predict that the Eigen
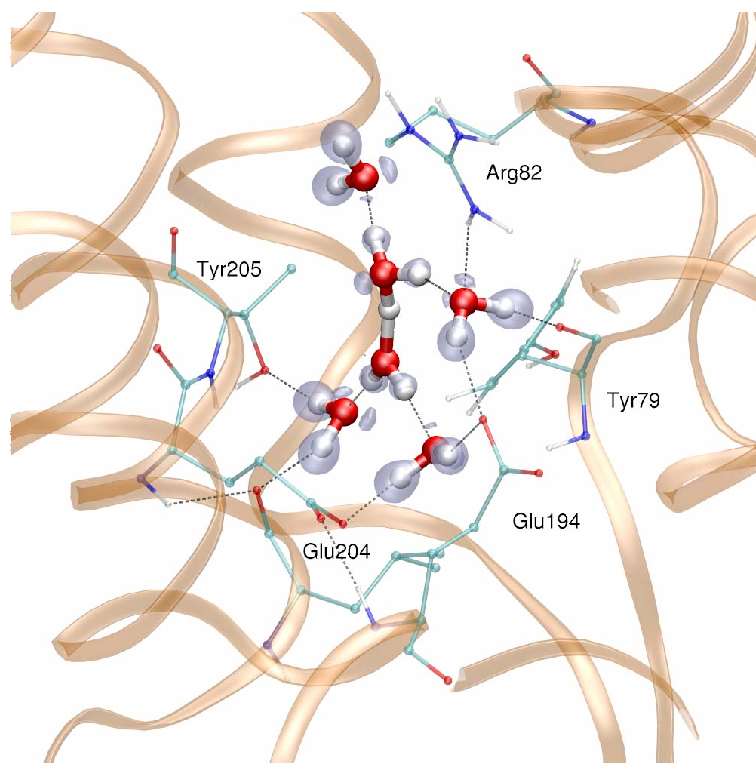
Figure 1.3: Image of the $H_5O_2^+$ cation (H in white, O in red) solvated by four water molecules in a side pocket of the bacteriorhodopsin molecule. Taken from D. Marx.[15]

$H_3O^+(H_2O)_3$ cluster embedded in the protein matrix can be stabilized for picoseconds and is more stable than the solvated Zundel $H_5O_2^+(H_2O)_4$ complex. Although many studies have offered informations about bacteriorhopsin and the proton pump process, the detailed microscopic nature of the proton translocation process remaines unclear. Furthermore, the hydroxide monohydrate anion $H_3O_2{}^-$ was studied in this thesis. This anion has a high dissociation energy of 1.2 eV, being a good model system for the study of strong low-barrier H-bonds which play an important role in enzymic catalysis.[3,19] One of the question that arises is: *what is the spectroscopic signature of these systems?*

Hydrogen Dihalides: Model Systems for Strong Hydrogen Bonds

The $X \cdots H \cdots Y^-$ (X, Y = halogens) systems represent the simplest strong hydrogen bonded complexes with binding energies above 0.7 eV ($> 6000\ cm^{-1}$) and may serve as good model systems for the study of strong hydrogen bonds. These systems have been extensively studied by photodetachment experiments by Neumark *et al.*[20] Photodetachment of the transition state precursor allows the study of the transition

state region of the neutral hydrogen transfer reaction between two halogen atoms:

$$X + HY \rightarrow XHY^{\#} \rightarrow XH + Y \tag{1.1}$$
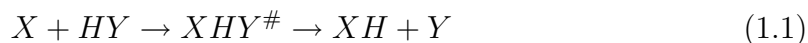
A detailed knowledge of the equilibrium geometries, vibrational frequencies and dissociation energies of the precursor anions allows for an improved description of the approximate anion potential energy surfaces used in simulations of the photodetachment process.

The detachment of an asymmetric precursor anion, i.e. photodetachment of vibrationally cold $BrHI^-$ provides Frank-Condon overlap with the exit channel of the corresponding hydrogen transfer reaction, not the saddle region of the transition state as shown by Neumark *et al.*[20,21] In principle, it is possible to prepare the anion in a vibrationally excited state which provides Frank-Condon overlap with the transition state,[22] however, this requires the knowledge of the vibrational signature of the anion precursors. The photodetachment of asymmetric anions to the transition state leads to two dissociation channels with different branching ratios. Mechanisms for the enhancement of the fragmentation ratio of one of the photodissociation products have been proposed theoretically for the symmetric and the asymmetric anions by Elghobashi *et al.*[23–27] by using few cycle IR + UV bond selective dissociation schemes. In these schemes, the exact knowledge of the vibrational frequency of the hydrogen motion is very important.

Vanadium Oxide Catalysts

Vanadium oxide based catalysts are used in the production of important chemicals, e.g., sulfuric acid H_2SO_4, maleic and phthalic anhydride and in the reduction of gas emissions from environmental plants (nitrogen oxide from flue gas of power plants). Most catalysts based on vanadium oxide consist of vanadium oxide films deposited on the surface of oxide supports, such as SiO_2, Al_2O_3, TiO_2 and others.[28] The advantage of supported vanadium oxides lies in the variability in the geometric and electronic structure of surface vanadium oxides. During the last decade scientists have shown that the activity and selectivity of supported metal oxide catalysts are significantly affected by the properties of the supported oxide material. For example, in the selective oxidation of methanol to formaldehyde, the turnover frequency (TOF)[a] is strongly influenced at the change of the composition of the support indicating that the oxygen in the $V - O - support$ bond is critical in the catalytic oxidation process.[28]

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[a]Number of molecules reacting per active site in time unit

Vanadium oxides play an important role as catalysts also in the selective reduction of nitric oxide to ammonia which is an environmentally significant reaction.[29–31] Another important reaction is the oxidation of the toxic carbon monoxide on powder vanadium pentoxide catalysts.[32] Vanadium oxides have attracted attention not only due to their catalytic activity, but also due to other important industrial applications. In this sense, VO_2 is one of the most studied system. It presents a insulator-to-metal transition at $68°C$. Below $68°C$ VO_2 has a high IR transmittance whereas above this temperature it becomes a metal and is highly reflective. Consequently VO_2 can be used for infrared active coatings.[33] VO_2 thin films have been proposed also as IR optical switching devices.[34] Permanent erasable holographic storage was investigated as well in a VO_2 film by using the changes in the optical properties at the phase transition.[35] V_2O_5 presents a similar transition from semiconductor-to-metal at $257°C$ with a higher infrared transparency as VO_2.[33] The transition temperature of VO_2 is much lower than of V_2O_5, however, the potential of applications would be enhanced if the temperature would be shifted to room temperature. Lowering of the phase transition temperature can be achieved by replacing oxygen atoms with fluorine VO_xF_y or by metal substitution with Ta, Mo, W and Nb.[33] Vanadium oxide thin films were proposed for gas sensors, e.g., ethanol sensors, as well. When vanadium oxides are in contact with some toxic or flammable gases, their surface conductance changes, indicating the presence of the gas.[36]

Despite of the industrial importance of vanadium oxides, most of their microscopic properties are still not well understood. The identification and characterization of the active sites in catalysis, with currently available surface science techniques remain challenging and gas phase studies can provide important information. Collision induced dissociation experiments[37] have shown that VO_2, VO_3 and V_2O_5 units are the main building blocks of vanadium oxide cationic clusters. Reactivity experiments demonstrated that the additional oxygen atom in the oxygen rich systems is the reactive site in the hydrocarbon reactions.[37,38]

From theoretical point of view, it has been shown that density functional calculation are well suitable for the characterization of the structure and of the vibrational frequencies of the vanadium oxide systems.[38–42] However, DFT calculations give usually higher values as the experimental ones[39,41,42] and therefore the calculated frequencies have to be scaled by constant factors. Although the DFT methods perform satisfactorily in the study of larger vanadium oxides, Nakao *et al.*[43] demonstrated the multi-reference character of vanadium monoxide. Multi-reference calculations which present a better agreement with the experiment were performed by Pykavy *et al.*[44,45]

for the $VO^{+/0/-}$ and the $V_2O_4^{+/0/-}$ systems. However, these simulations are very time consuming and can be applied only to small systems.

The thesis is outlined as follows: After the introduction, the experimental setup is described in Chapter 2. This chapter includes the description of the ion guiding tandem mass spectrometer, as well as of the Free Electron Laser for Infrared eXperiments (FELIX). Theoretical models used in the experiments are presented in Chapter 3 which includes basic concepts of infrared spectroscopy and the excitation mechanisms. The results obtained with this two methods on the strongly hydrogen bonded symmetric and asymmetric hydrogen dihalides as well as on the protonated water cluster ions and the solvated hydroxyl anion are presented in Chapters 4 and 5. In both these chapters, comparison of the experimental results with simulated spectra is performed where it is possible. Chapter 6 presents theoretical and experimental results on selected vanadium oxide cations. The thesis ends with Summary and Outlook, where a short summary of the results is given and future research plans are presented.