

# Chapter 7

## Summary and Outlook

### Summary

In the experiments presented in this thesis, the IR spectra of strongly hydrogen bonded ions and vanadium oxide cluster cations were investigated. Furthermore, high level calculations were performed in order to study the influence of the rare gas atoms *He* and *Ar* on the IR spectrum of  $VO^+$ .

This work was motivated by the importance of strong hydrogen bonds in understanding special characteristics of liquid water such as the high proton mobility. Hydrogen bonds play an important role in the secondary structure of proteins and in the enzyme catalysis as well. Vanadium oxides are known to have a significant role in the heterogeneous catalysis, but also in other industrial applications such as IR coatings, sensors and optical devices. Despite of the importance of these systems, many of their microscopic properties are still not well understood. The spectroscopic study of these systems in solid phase or on the surfaces is influenced by their environment, hence, their study in the gas phase offers important information.

The experimental approach employed for the investigations presented in this thesis relies on the combination of an ion guiding tandem mass spectrometer with an intense, tunable IR laser. For this, the apparatus was transported a few times every year to the FELIX facility located at the FOM-Institute for Plasma Physics, Rijnhuizen, the Netherlands. The interaction of the IR radiation with the gas phase ions occurs in a radio frequency temperature adjustable hexadecapole ion trap. The approaches on which the successful IR spectra measurements rely are referred to as "action spectroscopy", and are based on measurements of the dissociation products formed in the ion trap after irradiation as a function of the laser frequency. Two types of "action spectroscopy" were used, namely the IRMPD and the VPD methods. The IRMPD

technique is usually multiphotonic and is suitable to systems with low dissociation energies. The VPD spectroscopy is based on the messenger atom technique where a rare gas atom is weakly bonded to the molecule. The IRPD process relies on the photodissociation of the rare gas atom. The VPD method requires only few photons, often only one photon, for photodissociation. This makes the VPD technique applicable also for systems with high binding energies (higher than few  $eV$ ). Combination of the VPD method with the tandem mass spectrometer allows the measurement of the IR spectra of gas phase ions with increased sensitivity and selectivity.

The investigation of strongly hydrogen bonds was divided into two parts, namely the three atomic hydrogen dihalides and the protonated and deprotonated water clusters. In the first experiments presented in this thesis, the IR spectra of symmetric hydrogen dihalides  $BrHBr^-$  was measured by both IRMPD and VPD techniques. The experimental results support a symmetric hydrogen bond. The IR spectra show many combination bands between the symmetric stretch  $\nu_1$  and the antisymmetric stretch  $\nu_3$  which have a higher intensity than the fundamental  $\nu_3$  stretch. This indicates a strong anharmonicity of the PES and, hence, a complete breakdown of the harmonic approximation already at low quantum numbers. From the combination bands an indication of the value of the infrared inactive mode  $\nu_1$  could be obtained. The VPD spectra are in excellent agreement with the theoretical predictions. The understanding of the IRMPD spectra is more challenging. IR spectra measurements of larger  $BrHBr^-(HBr)_{1,2}$  ions indicate the destruction of the symmetry of the hydrogen bond at the addition of  $HBr$  units to the  $BrHBr^-$  core. The investigation of the IR spectra of strong hydrogen bonded systems was continued by a stepwise increase of the complexity of the studied systems. Thus, the IR spectra of the asymmetrically hydrogen bonded  $BrHI^-$  anion were studied in the region of the hydrogen stretches. The spectra of this ion show a higher complexity than for the symmetric  $BrHBr^-$ . High level calculations indicate strong coupling between all vibrational modes. The peak intensities are influenced by Fermi resonances. The results obtained from VPD and IRMPD studies together with theoretical calculations on this anion replaced the previous assignment of the bands from matrix experiments. Furthermore, the first IR spectra of protonated ( $H_5O_2^+$ ,  $H_7O_3^+$ ,  $H_9O_4^+$ ) and deprotonated ( $H_3O_2^-$ ) water clusters in the region between 500 and 2000  $cm^{-1}$  were measured. The experimental and theoretical investigation on protonated water clusters are challenging due to the flat PES on which the  $H$  atom executes large amplitude oscillations and to the strong coupling between the shared proton vibrations and modes involving the water monomers. The Zundel cation  $H_5O_2^+$  has a symmetric hydrogen bond between

two water molecules. The IRMPD spectrum was compared to previous high level calculations and to more recently performed experiments which used the multiphoton photodissociation and the messenger atom techniques. The assignment of the IR spectrum is controversy and requires further theoretical studies which address the experiments directly.  $H_7O_3^+$  and  $H_9O_4^+$  have a predicted Eigen type structure with the  $H_3O^+$  core solvated by three water molecules. Surprisingly, our studies reveal absorption of these systems at low energies, in contradiction to harmonic theoretical predictions. Additionally,  $H_9O_4^+$  shows an IR spectrum in the low energy region very similar to the features observed in the IR spectrum of the Zundel cation ( $H_5O_2^+$ ). The IRMPD spectra presented in this thesis together with the very recent VPD spectra which were recorded between 1000 and 4000  $cm^{-1}$  indicate a sensitive response of the IR spectrum to symmetry breaking of the hydrogen bond. This might explain the lack of sharp features in the IR spectrum of the hydrated proton in the bulk. Another very interesting system is  $H_3O_2^-$ , which is a good model system for the study of strong low-barrier hydrogen bonds which play an important role in enzyme catalysis. The predicted barrier of the double well minimum is much lower than the zero point level. The IR spectrum of this system is very complex and reveals broad bands. Tentative assignments of the observed features were proposed based on recently published VPD and simulated spectra.

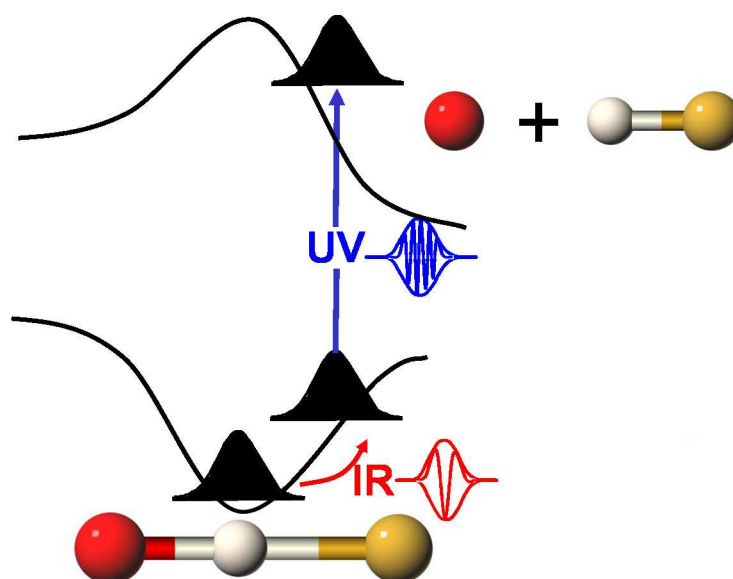
The second part of the results focuses on the investigation of vanadium oxide cluster cations. Experimental as well as theoretical studies have been performed. Theoretically, the influence of the rare gas atoms *He* and *Ar* was studied by multi-reference methods. The calculations predict a bent structure with the rare gas atom bound to the vanadium atom. The predicted dissociation energies are surprisingly high. The results indicate that one photon is sufficient for the dissociation of the *He* complex, whereas at least four photons are required for the dissociation of the *Ar* complex. Nevertheless, the predicted influence on the vibrational spectrum of  $VO^+$  at the attachment of one rare gas atom to the  $VO^+$  core is small. The vibrational analysis predicts a very good agreement for the frequency of  $VO^+ \cdot He$  with the experiment. The experimentally observed blue shift of 10  $cm^{-1}$  for the *Ar* complex from the frequency of  $VO^+ \cdot He$  is higher than theoretically predicted shift and is probably caused by the multiphoton absorption process. Furthermore, the structure of several oxygen rich vanadium oxide cluster cations was probed by the IRMPD technique. Two characteristic regions were found. The frequencies below 900  $cm^{-1}$  are attributed to  $V-O-V$  stretches, whereas the frequencies above 900  $cm^{-1}$  are attributed to vanadyl  $V=O$  modes. The structural assignment of the IRMPD spectra of the studied

vanadium oxide cations is difficult due to the lack of theoretical investigations on these systems. Here, the IRMPD spectra of the  $V_4O_{10}^+$ ,  $V_3O_8^+$  and  $V_6O_{15}^+$  cations were presented and discussed. The results suggest that the experiments probe the minimum geometry and not the structure with the lowest dissociation energy as proposed previously. Furthermore, the IRMPD spectra on  $V_3O_8^+$  suggest that the experiments probe the structure of two different isomers.

The results presented in this thesis demonstrate that IRPD studies combined with the FELIX radiation succeed in accessing the vibrational spectroscopy of cations and anions over a wide size range, and in particular can be applied to systems with as few as three atoms. It is therefore an ideal method for observing the size-dependence of the vibrational spectroscopy of cationic and anionic clusters over an extended frequency range that was previously inaccessible. In the case of the hydrogen bonded clusters studied here, the inclusion of anharmonic effects are a prerequisite for an adequate theoretical description of the IR spectra of these species.

## Outlook

The results presented in this work open new perspectives for future experiments. Studies of the transition state of the  $XHY^-$  ( $X, Y =$  halogens, oxygen) type anions by the Negative-to-Neutral-to-Positive (NeNePo) spectroscopy are planned for the near future. In these experiments, the transition state on the potential energy surface of the reaction  $XH + Y \rightarrow (XHY)^\ddagger \rightarrow X + HY$  can be reached by photodetachment of the electron with a femtosecond laser pulse referred to as *pump pulse*. The produced wavepacket motion can be monitored by a second femtosecond pulse referred to as *probe pulse*, delayed by  $\Delta t$  from the first one, which ionizes the molecule. By recording the cation signal as a function of the delay time, the motion of the wavepacket in the region of the transition state can be monitored in real time. The photodetachment of asymmetric anions provides Frank-Condon overlap with the exit channel of the corresponding hydrogen transfer reaction and not with the saddle region of the transition state. Thus, the molecule may dissociate through two fragmentation channels with different branching ratios. Methods for the optimization of one of the dissociation channels were proposed theoretically for symmetric and asymmetric anions by Elghobashi *et al.*<sup>23-27</sup> by using few cycle IR + UV bond selective dissociation schemes as shown in Figure 7.1. In these experiments one IR pulse is used in order to move the proton closer to one of the halogen atoms and at the right delay time a second ultrashort UV pulse photodetaches one electron. The motion of the wavepacket on the PES of the neutral systems is monitored by a third pulse (probe



**Figure 7.1:** Schematic representation of the few cycle IR + UV bond selective dissociation scheme for the control of the branching ratio of different dissociation channels when the saddle point is reached by photodetachment. Received from N. Elghobashi.<sup>171</sup>

pulse) which ionizes the molecules. In this way, optimizations of the desired reaction path are possible. By the experiments proposed here, in addition to the knowledge accumulated on the anionic system, information about the potential energy surface of the neutral, especially of the transition state, can be obtained in real time and the optimization of the preferred photodissociation product can be achieved.

