Chapter 9

Summary and Outlook

In this thesis, the vibrational spectroscopy of mass selected cluster ions in the gas phase has been investigated by photodissociation spectroscopy using the free electron laser FELIX. Structural and electronic characterization of different types of clusters has been achieved, establishing this method as one of the most generally applicable tools for characterizing clusters experimentally. Most of the results presented in this work are the first infrared spectra of the corresponding species.

The infrared spectra of collisionally cooled, mass-selected, vanadium oxide cluster anions were measured for species ranging from $V_2O_6^-$ to $V_8O_{20}^-$ and cluster structures are identified through a comparison with simulated spectra based on harmonic frequencies and intensities from density functional theory calculations. In general, the agreement between simulated *linear* infrared spectra and experimental *multiple photon absorption* infrared photodissociation spectra is sufficient to identify a single electronic and structural isomer responsible for the main absorption features. From this extensive study, infrared multiple photon photodissociation emerges to be a technique well suited to the characterization of medium sized clusters. For clusters consisting of less than a dozen atoms, the messenger atom technique is preferable and it becomes necessary for species smaller than $V_2O_6^-$, the smallest cluster that could be photodissociated with full FELIX power. The larger clusters studied here show broad absorptions, but this is attributed to intrinsic anharmonic coupling and not to the particular experimental technique.

Evidence for size-dependent charge localization is found in the $(V_2O_5)_n^-$ clusters (n=2–4). Symmetry-breaking localization is observed in many other chemical systems for the reverse process—creation of an electron hole. The proper description of electron (hole) localization phenomena by density functional theory depends on the functional used, and in particular on the admixture of Fock exchange. The present infrared photodissociation spectra are therefore a benchmark for density functional theory functionals, for determining the correct functional to be employed. Even though the largest cluster anion studied here, $V_8O_{20}^-$, is still rather small, it reveals some striking

similarities to the properties of a vanadium oxide single-crystal surface [125], making it an interesting gas-phase model for surface adsorption and reactivity studies.

Currently, $V_4O_{10}^+$ is the largest vanadium oxide cluster cation for which a definitive structural assignment is given by comparison of experimental data on selected clusters with theory. In the future, it will be interesting to extend IR-PD studies to larger vanadium oxide cluster cations and search for clusters with marked similarities with the spectra from the condensed phase, as it was observed in the case of the anion $V_8O_{20}^-$. Definitive structural assignment both in positive and negative charge states is currently available only for three clusters: $V_2O_6^{+/-}$, $V_3O_8^{+/-}$, and $V_4O_{10}^{+/-}$. The knowledge of the structures of larger vanadium oxide cluster cations will also allow for a better comparison with the known negative counterparts in order to further elucidate the influence of charge status on cluster structure.

For the aluminum oxide cluster cations the infrared spectra demonstrated that the corundum derived structure of $(Al_2O_3)_4^+$ gas-phase clusters is not the global minimum. The global minimum structure has no common features with any of the known bulk phase Al_2O_3, contrarily to previous assumptions and calculations. The similarity of the calculated spin density for this species to the one calculated for $V_4O_{10}^+$ makes $(Al_2O_3)_4^+$ a candidate for further reactivity studies, for example, in the activation of methane [184]. Our infrared spectra demonstrated the potential of a genetic algorithm newly developed by M. Sierka (Humboldt-Universität zu Berlin), and based on these results, a new structure has been proposed also for the neutral $(Al_2O_3)_4$ [287]. These results show that the localization of the positive charge in aluminum oxide cluster cations can have a dramatic effect on their structure, which is different from vanadium oxide clusters, for example. Therefore, it will be interesting to further study aluminum oxide cluster anions, which are virtually unexplored.

The structures of smaller alumina oxide cluster cations are also found to be different from bulk-derived species, or from "chemical intuition". They are rather curved two-dimensional networks, based on hexagons of alternating aluminum and oxygen atoms. A space tessellation based on planar hexagons is flat but a curvature can be introduced if, for example, some hexagons share three atoms instead of two (see the structure of $Al_9O_{13}^+$). At larger cluster sizes the initially open cage structures may close and/or bulk-like structures may appear. Therefore, it will be of interest to explore larger aluminum oxide clusters looking for such characteristic structural changes. Moreover, only $Al_8O_{12}^+$ and the $(Al_2O_3)_{1-4}(AlO)^+$ series have been studied to date. The $(Al_2O_3)_n^+$ clusters are predicted to have lower symmetry than the studied closed-shell ones but it is currently unclear if one can describe general trends also for this series of cluster ions.

What is the contribution of these results to the understanding of heterogeneous catalysis? Looking for models for support material among these non bulk-like structures may appear questionable. However, real macroscopic catalysts are seldom bulk pieces but rather nanostructured assemblies. Also, vibrational spectroscopy studies

of thin Al_2O_3 films [149–151], which are often used as support materials, found that the corundum structure is not the most stable one. It is therefore appropriate to suppose that precisely these unexpected structures can play a key role in explaining the mechanisms of heterogeneous catalysis. Moreover, intramolecular interactions must be the same at whatever scale, whether it is a size range where every atom "counts" or a regime in which bulk structures are stable toward the addition or removal of particular atoms. The fact that "chemical intuition" is not capable of predicting correct structures is, after all, disappointing but not surprising. It recalls us that our understanding of interatomic potentials is limited. Clusters are therefore a privileged arena to test our hypothesis and improve our tools.

By adapting a dual target laser vaporization source to the experimental apparatus, we extended our studies to new species. The doping of vanadium oxide cluster anions with titanium atoms was effectively employed to modify the electronic configuration of clusters without changing the overall geometric structures. In the $V_{4-n}Ti_nO_{10}^-$ series the structures do not significantly change from $n{=}0$ to $n{=}3$, while different electronic structures are found. Moreover, not only the number of unpaired electrons can be modified but also their site specific localization, while preserving the geometrical structure. Except for the symmetry lowering due to the titanium atoms, the structures of the $(V_2O_5)_{n-1}(VTiO_5)^-$ ($n{=}2$–4) clusters are found to be the same as in the corresponding vanadium oxide cluster anions $(V_2O_5)_n^-$ ($n{=}2$–4), while the number of electrons is reduced by one, yielding closed-shell electronic structures.

In the future, the dual target laser vaporization source should be exploited in combination with reactivity studies. Of particular interest are series of experiments where the reactivities of different electronic structures for a fixed geometry are investigated. Conversely, a complementary strategy could be pursued, in which the element substitution drastically changes the geometry of the species of interest. For example, doping vanadium oxides with alkali metals could be used to break the cage structures found in larger anions. Apart from these "electronic and geometric engineering" experiments, studying the interaction of two different oxides is also of great interest. However, the species created in the plasma of the dual target laser vaporization source are likely to be in the most stable conformation. Since these are not necessarily the species that one intends to study, the source should be modified, introducing a larger space between the two targets. This would allow, for example, vanadium oxides to be deposited on pre-formed aluminum oxide clusters.

Preliminary results on the spectroscopic characterization of reaction intermediates (see Appendix A) have shown further potentials of infrared photodissociation spectroscopy. However, a serious problem is posed by the coexistence of several species in the ion trap. A solution to this problem requires the construction of a second ion trap and another mass selection stage. Reaction products could then be mass selected and trapped again, decoupling the reaction cell from the photodissociation region.

Infrared photodissociation has been successfully applied to the study of solvated

ions. The selectivity of the method allows for probing the evolution of hydrogen bonding networks adding one molecule at a time. Infrared spectra of gas phase solvated multiply charged anions provide new insights into the structure of these complexes. Overall, from the observed vibrational frequencies of both the dianion and the solvent, the complexes can be seen as a distorted tetrahedral SO_4^{2-} core surrounded by H_2O molecules. No evidence for low-frequency ($\sim$1000 cm^{-1}) stretch and bend frequencies associated with a shared proton is observed, in contrast to singly-charged cations and anions with strong hydrogen bonds such as $H_5O_2^+$ and $H_3O_2^-$ [231, 264]. The absence of such features reflects the delocalization of negative charge in the sulfate ion over the four oxygen atoms, so that the individual hydrogen bonds with the surrounding water molecules are weaker than in singly-charged species with strong hydrogen-bonds. Evolution of the water solvation shell can be clearly followed in the spectroscopic signature and shell closing is found for twelve water molecules.

A crucial detail of the method used in this work is the adiabatic cooling of the clusters achieved by many collisions with cold helium buffer gas in the ion trap. Adiabatic cooling suppresses the contribution of kinetically-trapped metastable isomers to the measured spectra, substantially simplifying the interpretation. The advantage offered by the present technique is demonstrated in the case of the hydrated electron clusters. In previous studies, clusters were frozen in supersonic expansions and evidence was found for at least three isomeric classes [21]. Contrary to this, we found no indications for different isomers, although exactly the same cluster source as in Reference [21] was used. The infrared spectra of hydrated electron clusters show that the electron binding in the clusters up to n=20–25 is dominated by the AA-binding motif, i.e., the predominant binding to a single water molecule, which is dipole-oriented and points two hydrogen atoms into the electron cloud. The AA-binding motif contributes to the infrared spectrum up to n=50, suggesting that it remains an important binding motif, also in much larger clusters than previously believed. Starting between n=20 and n=25, other water molecules directly interact with the additional electron, suggesting the onset of the formation of a cavity near the surface of the cluster. As the cluster grows, the AA motif remains but part of the electron density is now delocalized over multiple water molecules. No abrupt changes in the spectra are observed in the range from n=15 to n=50, supporting the notion that the transition from an externally to internally solvated electron is gradual, as originally suggested by Coe et al. [19, 22]. Although vibrational spectroscopy yields important insight into the binding motif of the hydrated electron in finite clusters, characterization of these species emerges as a particularly difficult task for infrared spectroscopy. This is due to the fact that the electron is bound to several water molecules and these structures do not give rise to any particular signature, except for small clusters.

A desirable modification for the tandem mass spectrometer regards the mass range of the quadrupoles. Quadrupoles capable of selecting masses up to 4000 Daltons are commercially available. This extension will be of particular interest for the studies

on solvated ions for two reasons. First, the largest water cluster currently selectable has 55 water molecules. The pH of a proton solvated in such a cluster is zero.[1] In this size range the addition of a single water molecule significantly alters the pH of the "solution". Increasing the cluster size beyond 55 water molecules allows for studying a size range that is more similar to common solutions. Second, in cold neutral water clusters the onset of crystallinity occurs somewhere between 200 and 1000 water molecules [283]. Smaller water clusters correspond to quasi spherical nanoparticles with a crystal interior and a disordered "reconstructed" surface [284], as a result of their tendency to minimize dangling bonds, while smaller clusters contain only "surface" water molecules. It will be interesting to explore these transitions in the spectra of solvated ions. With respect to the crystallization issue, it is of interest to measure the vibrational spectra of clusters at different temperatures.

Vibrational spectroscopy in the 500–2000 cm^{-1} region accesses directly the strong proton transfer modes, water libration and bending modes. Another water libration mode is found at $\sim$400 cm^{-1} and the frustrated translations of water molecules in a hydrogen bonding network are located at about 200 cm^{-1}. Extension of the experiments to this spectral range will yield further insight into the structure of these systems.

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[1]pH$=-\log[\mathrm{H}^+]$, where [H^+] is expressed in mol/liter. A liter consists of $\sim$55 moles of water. Therefore, a number ratio of 1 to 55 corresponds approximately to a 1 M solution.