

Introduction

Vibrational spectroscopy has been a standard method for structural characterization of condensed phase samples for many decades. However, the application of vibrational spectroscopy to gas phase ions poses two main experimental challenges. First, the low number densities of ions attainable in the gas phase—roughly less than one million per cubic centimeter—generally prohibit direct absorption measurements. Second, most of the characteristic infrared transitions lie in the fingerprint region (500 to 2000 cm^{-1}) of the electromagnetic spectrum, a region which cannot be continuously covered with the required intensity using commercially available infrared radiation sources.

The main goal of this work is the characterization of the geometric and electronic structure of mass-selected gas phase cluster ions through vibrational spectroscopy, applying a novel experimental method developed in the Asmis–Wöste group. The fundamental premise for this method is the correlation of molecular structure with a characteristic “fingerprint” within the vibrational spectrum and its assignment based on a comparison with the simulated spectra of possible candidates. The properties of isolated gas phase clusters are simpler to calculate than those of the same species embedded in a complex environment. Consequently, higher level computational approaches can be applied, leading to more accurate and reliable results. Conversely, experimental results can be used as benchmarks for testing models aimed at describing the more complex systems. Moreover, once cluster properties in the absence of any external perturbation are known, interactions with the environment, e.g., the solute-solvent interaction, can be studied in a sequential manner by adding one solvent molecule at a time.

The experimental setup consists of a tandem mass spectrometer, which allows trapping, cooling and probing of mass selected gas phase ions. Energy is deposited in cluster ions when irradiated with high intensity infrared laser light by the absorbed photons, given that the laser wavelength is resonant with a vibrational transition. This can eventually lead to cluster dissociation, so that photon absorption can be indirectly detected by monitoring fragment yields. This technique, known as infrared photodissociation spectroscopy, is described in Chapter 1. The experimental setup is presented in detail in Chapter 2. All experiments were performed at the FOM Institute for Plasma Physics Rijnhuizen (Nieuwegein, The Netherlands) using the free

electron laser FELIX.

Results obtained from these experiments are divided into two main topics. Results on *metal oxides* are presented in Chapters 3 to 5. Results on *solvated ions* are presented in Chapters 6 to 8. An introduction to each system is to be found at the beginning of the corresponding chapter. A general overview of these two distinct subject areas will now be given.

Metal Oxides

The focus of the first part of this work is on metal oxide aggregates. They are intensely studied because of their relevance as building blocks for nanostructured materials. One of the most intriguing aspects of these nano-sized aggregates is their pronounced size-dependent properties as well as their sensitivity to the immediate environment as a result of their large surface-to-volume ratio. In particular, vanadium oxides are important in a diverse range of devices such as supported catalysts [1], cathode materials in lithium batteries [2], in bolometric detectors [3], and as ferromagnetic nanotubes [4]. Vanadium oxide-based catalysts are used in the production of important chemicals and in the reduction of environmental pollution. Vanadium is also the most important metal used in metal oxide catalysis [5–8]. The importance of vanadium in supported metal oxide catalysis is shown by Figure 1a. This figure shows the number of publications on several transition metals in the field of metal oxide catalysis in the period 1967–2000 as a percentage of the total number.

Most catalysts based on vanadium oxides consist of a vanadium oxide layer and/or one or more vanadium oxide cluster species deposited on the surface of an oxide support such as Al_2O_3 , SiO_2 , or TiO_2 (see Figure 1b). However, a detailed understanding as well as the computational simulation of the molecular structures and reactivities of these systems still raise considerable problems. First, the surfaces of real supported

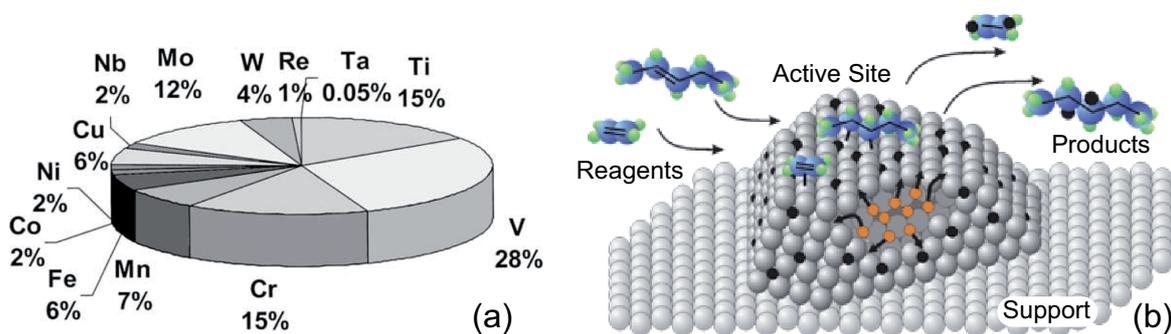


Figure 1: (a): Overview of the importance of vanadium in supported metal oxide catalysis. The numbers are based on a literature search in the period 1967–2000 [1]. (b): A sketch of a supported catalyst [9].

metal oxide catalysts are so irregular and inhomogeneous that advanced surface analytical techniques cannot be used effectively. Even model catalysts, accurately prepared under ultra-high vacuum conditions with a well known chemical composition, seldom have well defined structures (see, e.g., Figure 2). Second, the support was

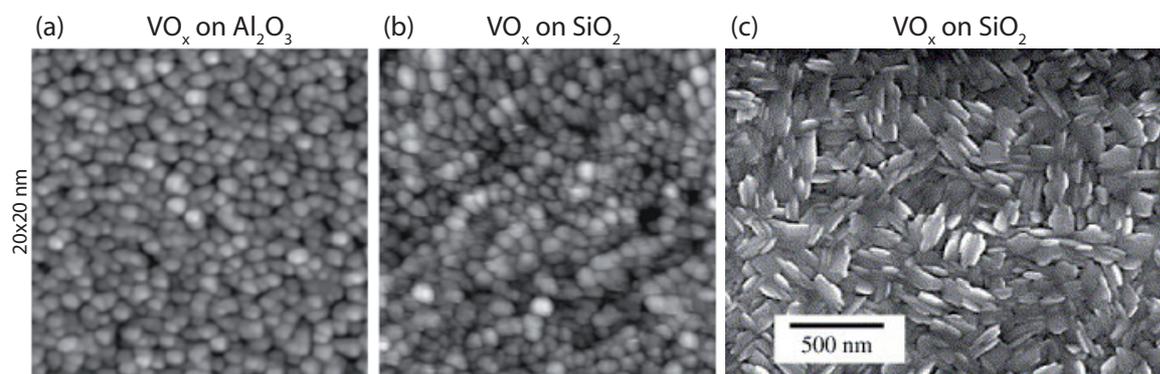


Figure 2: (a) and (b): 20x20 nm STM images of vanadium oxide particles deposited on alumina and silica, respectively [10]. (c): STM image of larger vanadium oxide particles deposited on silica [11].

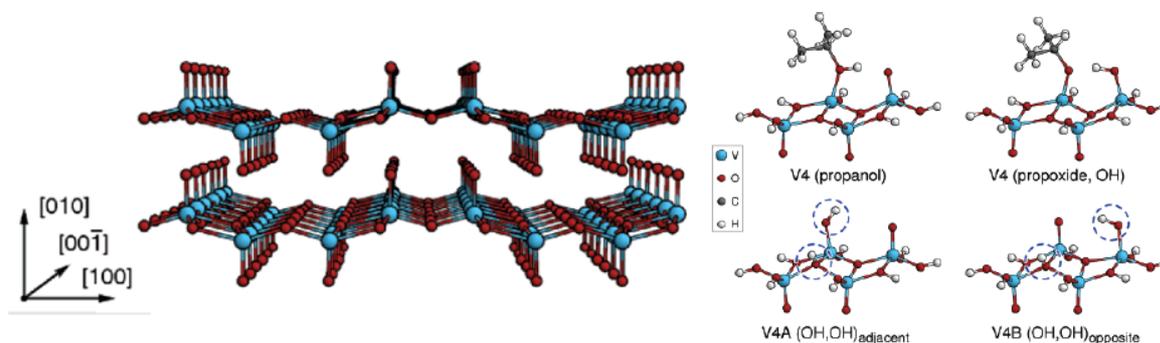


Figure 3: Left: Structure of the (010) surface of V_2O_5 . Right: Structures of energy minima on the oxidative dehydrogenation of propane pathways from calculations on clusters [12].

initially considered as an inert substance that provided a high surface area to carry the active metal oxide component or an improved mechanical strength for the catalyst material. However, during the last decades, it has been shown unambiguously that the activity and selectivity of supported metal oxide catalysts are significantly affected by the properties of the support oxide material. This is generally known as the metal oxide–support effect, although its exact origin and mechanism of operation is still unclear. Up to now, no consistent model can describe—in a quantitative manner—the

role of the structure or composition of support and the presence of specific promoter elements in terms of the electronic and/or geometrical structure of the supported catalyst [1]. Third, the great complexity of these systems impedes accurate theoretical treatment, so that typical calculations are restricted to simplified systems. For example, in the framework of reduced complexity, only one or few layers of vanadium oxide are considered, and the presence of a substrate is often neglected. Subsequently, a portion of the crystal is chosen that is small enough to be treated by available computational tools. Potential energy surfaces for adsorbed reagent molecules are then calculated only for these smaller systems (see, e.g., Figure 3).

Our experimental approach for shedding light on the relationship between geometric and electronic structure on the one hand, and observed reactivity patterns on the other, involves performing reactivity measurements combined with structural characterization on size-selected clusters and cluster ions in the gas phase. The strategy adopted in this work consists primarily of four steps: (*i*) determining the geometric and electronic structure of gas phase vanadium oxide cluster ions, as model systems for the active sites, (*ii*) of gas phase aluminum and titanium oxides as model systems for the support, and (*iii*) of compounds of vanadium oxides with either aluminum or titanium oxides, as model systems for the active site–support interaction; (*iv*) investigating the reactivity of these species with different molecules, e.g., with hydrocarbons, and studying the structure of reaction intermediates and products. All spectroscopic data obtained on metal oxide cluster ions are compared with DFT calculations carried out in the Sauer group (Institut für Chemie, Humboldt-Universität zu Berlin, Germany).

Each of the chapters in the first part of the present work is devoted to one of the afore-mentioned steps. In Chapter 3, the first infrared spectra of gas phase, mass-selected, vanadium oxide cluster anions are presented, corresponding to step (*i*). The structures of vanadium oxide cluster anions were, prior to this work, unknown. Here, geometric and electronic structural assignments are given for clusters from $V_2O_6^-$ to $V_8O_{20}^-$. Cage structures are found and charge localization with increasing cluster size is observed for the $(V_2O_5)_n$ series. Results on aluminum oxide clusters (*ii*) are presented in Chapter 4. Some calculations were available on aluminum oxide clusters in the literature, but no structural assignments based on experimental evidence for clusters consisting of more than six atoms has been reported preceding this work. New unexpected structures are found that are different from any bulk-like geometry and the structural evolution of the closed-shell $(AlO)(Al_2O_3)_{1-4}^+$ cluster ions is studied as a function of size. Mixed metal oxide clusters (*iii*) have never been studied before: our first exploratory experiments are presented in Chapter 5. In this chapter, the studies on mixed vanadium-titanium oxide clusters are presented and the possibility of modifying the electronic configuration of a cluster without transforming the overall geometry is explored. Reactivity studies (*iv*) are still in progress and preliminary results are presented in Appendix A. It is shown that infrared spectroscopy of reaction

partners is a new and powerful tool for investigating reaction mechanisms.

Solvated Ions

The second part of this work concentrates on hydrogen bonding. Hydrogen bonding governs a number of diverse interactions relevant for biology, chemistry, and physics, which range from the solvent properties of water and other liquids to the structure of proteins and nucleic acids. In these systems, the structures of the bare (unperturbed) molecular units composing the cluster are often known, but the intermolecular bonds and arrangements are often not clear, as well as the induced perturbations. The essential quantity required for a meaningful description of these systems is the interaction potential between the molecular constituents. However, such potentials are difficult to access because of the complexity of treating the thermal and quantum fluctuations of many atoms and at the same time providing a highly accurate description of both the strong and weak interactions. Hydrogen bonds are especially interesting from the point of view of cluster spectroscopy, which can probe how the properties of a collection of molecules held together by hydrogen bonds evolve with size.

Chapter 6 addresses the infrared spectroscopy of protonated ammonia clusters. The geometrical structure of these clusters is known from previous spectroscopic studies. New data are presented concerning a critical spectral region, where the proton responsible for hydrogen bonding is expected to be active, which is very difficult for theoreticians to simulate.

Chapters 7 and 8 address the hydration of two charged species, namely the sulfate dianion and the bare electron. A complete understanding of the elementary processes involved in ion solvation has eluded scientists for more than a century. Only in recent years has a clearer picture emerged of how solvent molecules respond to the presence of an ion to form solvation shells. In these chapters, vibrational spectroscopy is used to elucidate the structures and properties of ion–solvent complexes. Knowing the molecular structures allows for a deeper understanding of the delicate forces involved in the early stages of ion solvation.

The sulfate dianion is of fundamental interest, not only because of its relevance in ice nucleation in the troposphere, activity lowering in fuel cells, and regulation of metabolic processes, but also, because it poses basic questions regarding its own stability. The concept of a doubly negative molecule interacting along a Coulombic repulsive surface as two singly negative species seems to exclude any possibility of stable states. However, at some distances, chemical forces can lead to a local minimum in the potential energy surface and one may encounter a metastable dianion. For the bare sulfate dianion a local minimum does exist, but it is metastable with respect to autodetachment. The study presented in Chapter 7 probes the step-by-step evolution of the solvent network around the dianionic core, providing the opportunity to study

novel hydrogen-bonding motifs differing from those seen in the hydration of singly-charged anions and to test the validity of predictions.

The solvated electron in liquid water was first identified in 1962 [13]. Since then it has been found to be a ubiquitous species in aqueous radiation chemistry, a common product of the UV photolysis of many inorganic and aromatic molecules, and to play a prominent role in biologically relevant processes, electron transfer, and charge-induced reactivity [14]. Gas-phase clusters of water molecules have also been observed to carry an extra charge and they represent microscopic analogs to their bulk counterparts, assuming that sufficient solvent molecules are present. Spectroscopic studies of these clusters provide insight into the short-range interactions that are relevant to the structure of the aqueous electron in bulk liquid water. For water clusters, however, the critical size beyond which the cluster anion resembles the bulk hydrated electron has remained a controversial issue. On the one hand, early molecular dynamics simulations [15–18] predicted that the electron would be localized on the cluster surface for smaller clusters and inside the cluster for larger sizes. On the other hand, photoelectron spectroscopy [19–25], electron absorption spectroscopy [26], and vibrational spectroscopy [27–30] found three isomeric classes which coexist and evolve smoothly over a broad range of cluster sizes. In the study reported in Chapter 8, vibrational spectroscopy is applied to $(\text{H}_2\text{O})_n^-$ clusters with up to 50 water molecules, which are adiabatically cooled below 50 K.

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