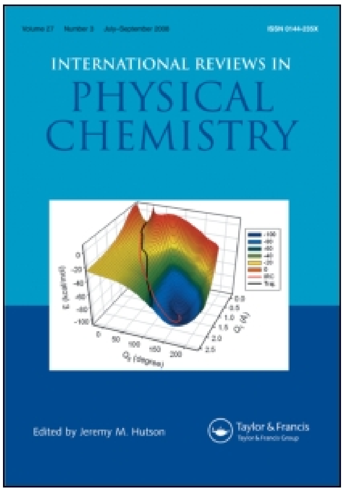

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Vladimir E. Bondybey; Martin K. Beyer

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How many molecules make a solution?

VLADIMIR E. BONDYBEY† and MARTIN K. BEYER
Institut für Physikalische und Theoretische Chemie, Technische Universität
München, Lichtenbergstraße 4, 85747 Garching, Germany

Water clusters are studied in order to investigate the evolution of solution phase chemistry from the molecular level to bulk. When water clusters are studied in a Fourier transform ion cyclotron resonance (FI-ICR) mass spectrometer, their fragmentation under the influence of infrared black-body radiation must be considered and can be used as a tool to monitor the destabilization of particular arrangements as a function of cluster size. As examples for solution phase chemistry, dissolution of acids, metal ion oxidation and metal halide precipitation, acid–base catalysis and hydrolysis are discussed. All these solution phase reactions proceed on the single-ion level in small water clusters. In accordance with spectroscopic and thermochemical data, gas phase ion chemistry of small water clusters rapidly approaches bulk behaviour, if the ion high concentration and pH value of the cluster are taken into account. Examination of competing reaction pathways as a function of cluster size in hydrated electron clusters reveals the crucial influence of entropy. Recent photodissociation experiments by Metz and Cocrorteers provide experimental evidence for the salt bridge mechanism for charge separation in hydrated dication clusters.

Contents

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† Email: bondybey@ch.tum.de

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1. Introduction

One of the major motivations for cluster research was always the desire to understand the transition from the properties of individual atoms or molecules to the collective behaviour of condensed phase systems [1]. Many early studies involved small clusters of metal atoms, with the underlying question of how many atoms form a metal, how big a particle has to be to exhibit all the typical characteristics of a metal [2]. Similarly, numerous gas phase studies appeared of aggregates of ionic species such as metal halides or other salts, and again the interesting question was how many of such molecules are needed to develop the properties of a bulk crystal [3, 4]. Clusters of this type, consisting of from just a few to several hundred discrete atoms or molecules, with sizes in the nanometre range and sometimes referred to as 'nanoparticles', often have fascinating properties and a number of potential technological applications [5].

Another area of lively current interest is clusters or aggregates of covalent molecules [6]. In our group we were recently interested in 'solvated ions', clusters consisting usually of a central ion with a number of attached solvent atoms or molecules [7–36]. Our research has shown, that in many respects, these systems can be viewed as 'nanosolutions', where many bulk liquid concepts, such as concentration [27], acidity or pH value [7, 24], are applicable and that numerous reactions well known from bulk solutions can be carried out and studied in microscopic detail in these finite systems. Analogues of ionic dissolution [7, 24, 27], neutralization [19, 21], reduction or oxidation [12, 14, 19, 21, 34, 35], precipitation [27, 33], hydrolysis [10, 31] and other types of processes [9, 16, 32] have all been examined in such clusters of solvent molecules. In view of these observations, one is surely entitled to ask 'how many molecules make a solution?'

Most of the processes proceeding in nature, as well as many chemical reactions important in industry, take place in solution. The Solvent can have a tremendous influence on the rate, and even the course and outcome, of a chemical reaction, and while in principle these effects are known, a detailed understanding is still missing. Finite, discrete clusters are theoretically more tractable than bulk systems, they are easily prepared and studied experimentally and they can provide a detailed insight into solution chemistry. By studying the behaviour of single ions in a solvent environment, cooperative effects are excluded [33], and the intrinsic reactivity of the solvated ion is probed.

Obviously, water is the most important solvent on Earth, and it is therefore not surprising that water clusters in particular, neutral as well as ionized, have been most widely studied, both by optical means [37–41] and by mass spectrometry [42–44]. Early high-pressure mass spectrometry investigations yielded a huge body of quantitative data on the hydration energies of most singly and many doubly charged ions as a function of the number of solvent molecules [45–47]. High-resolution optical spectroscopy was able to describe and characterize completely many neutral and a few charged water clusters consisting of up to 10 water molecules [37–41].

In addition to pure water clusters, the number of solutes studied in aqueous environment by spectroscopic techniques grows rapidly. The selectivity of cation-π interactions have been probed in water–benzene clusters by Lisy and coworkers [48]. Conformations of biomolecules in water clusters are studied by Zwier and coworkers [49]. Metal ion–water interaction is probed in zero energy kinetic electron pulsed field ionization (ZEKE-PFI) spectroscopy by the group of Duncan [50].

The potential of cluster research to unearth solution phase reaction mechanisms is currently undergoing rapid development [51, 52]. A fruitful interaction between experimental work and theoretical modelling helps in the identification and characterization of the key effects and processes underlying aqueous chemistry. Many of these earlier studies have tackled the question of this review's title in a way which was recently outlined in this journal by Coe [53], who connects the properties of aqueous clusters, such as hydration enthalpies and electron affinities, to bulk. Recent studies by Wang and coworkers [54], who extrapolate photoemission features of hydrated doubly charged anion clusters, with an overview of earlier efforts given by Stace [55], go in the same directions.

This invited review gives us the opportunity to discuss some results of our own Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometric studies and quantum chemical calculations in the broader context of the field. After a description of the experimental apparatus and procedures developed in our group, we will describe a variety of reactions and processes in clusters with up to 100 water molecules, which clearly exhibit the behaviour characteristic of bulk solutions, although in a somewhat different manner to the quantitative approaches discussed above. Instead of trying to deduce measurable bulk quantities such as hydration enthalpies or band gaps from cluster data, our results focus on the chemistry. We are going to show that bulk chemical behaviour is regularly exhibited by clusters containing on the order of 10 water molecules, the same number given by Stace [55] for extrapolating bulk solvation phenomena from gas phase thermochemical values. Our recent studies of hydrated electrons [32] have revealed that, in addition to simple thermochemistry, entropic effects are also quite important, and this topic in connection with many cluster processes will also be discussed in one of the following sections. While our experimental methods usually address singly ionized clusters, in bulk solutions multiply charged ions are also common, and we have recently used density functional theory to examine the problem of a charge-reduction process in clusters via a novel 'salt bridge' mechanism [20], which was even more recently confirmed through experiments by Metz and coworkers [56, 57].

As in the case of metals or crystals, in the case of 'nanodroplets' the answer to the question 'how many molecules make a solution?' depends on the property or reaction one is investigating. As we discuss various problems and systems in the following sections, we will try to find or at least to suggest answers to the above question.

2. Experimental set-up

2.1. *FT-ICR mass spectrometer for cluster studies*

The experiments in Garching to be described in the following sections were carried out with a Bruker/Spectrospin CMS47X FT ICR mass spectrometer [58–61] displayed schematically in figure 1. The instrument employs a cylindrical 60 mm × 60 mm *infinity* cell [62] located within a 15 cm room temperature bore of a 4.7 T superconducting magnet. It is fitted with an external ion source and transfer optics and a differentially pumped ultrahigh-vacuum (UHV) system. The experiment is controlled by an ASPECT 3000 minicomputer. The apparatus was modified [60, 63] in our laboratory specifically for cluster studies, and an additional chamber and differential pumping stage were added to allow operation with molecular beam ion sources.

The ions are produced in a supersonic expansion source attached to the external source chamber. The molecular jet emerging from the source is shaped by a 1.0 mm skimmer (Beam Dynamics Inc.), which separates the source chamber from the next differential pumping stage. The beam is accelerated to 3 keV and guided, through two additional flow constraints and differential pumping stages, into the homogenous high-field region of the magnet, where it is stepwise decelerated below the trapping potentials. For enhanced ion trapping efficiency, the Caravatti method [64] may be used. In this method, a small potential gradient is applied perpendicular to the velocity of the ions, converting part of their kinetic energy into the cyclotron and magnetron motion perpendicular to the magnetic field axis.

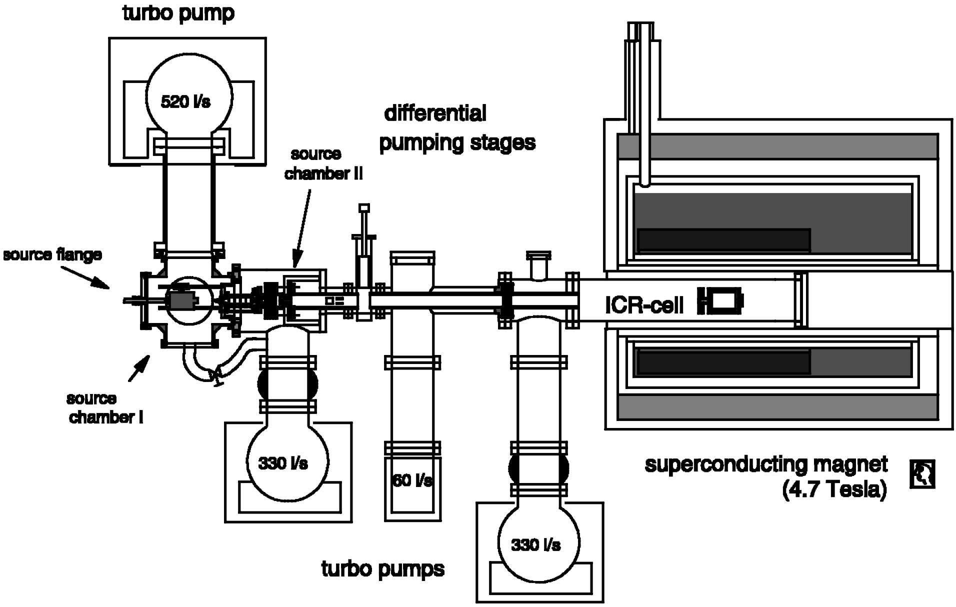

Figure 1. Side view of the Garching FT ICR instrument. Ions are produced in the source chamber and transferred to the ICR cell inside the magnet by a system of electrostatic lenses. Four differential pumping stages allow the application of molecular beam sources with a high gas load. Reproduced with permission from reference [58]. © 1995 American Institute of Physics.

The UHV turbomolecular pumps are shielded against the high stray field of the magnet with soft iron; the rotary roughing pumps are operated without shielding. The minimum pressures reached without gas load are 5×10^{-7} mbar, 8×10^{-8} mbar and 1×10^{-10} mbar in the first, second and fourth stages of differential pumping respectively. The reaction gas is introduced optionally into the UHV region via two sapphire–gold-sealed needle valves. For cleaning purposes, the gas inlet system can be evacuated by a rotary pump. The UHV region, the needle valves and the UHV turbomolecular pumps are routinely baked out.

The pressures in the source chamber, the second region and the UHV region are measured by Penning ionization gauges. The Penning gauge in the UHV region is placed 80 cm away from the ICR cell directly on top of the turbomolecular pump and shielded against the magnetic field. When a collision gas is introduced into the cell, the constant background pressure represents a stationary state determined by the gas flowing into the cell, the atoms and molecules adsorbing and desorbing from the apparatus walls and the pumping. All these processes are highly dependent on the specific nature of the gas, and the actual pressure in the cell is different from the pressure above the pump where the Penning ionization gauge is placed. The pressure determined by the Penning ionization gauge is therefore corrected by an empirical geometry factor and the sensitivity of the ion gauge [65].

A Bruker ASPECT 3000 minicomputer is used for experiment control and data processing. The processor has limited multitasking capabilities. It is equipped with 768 kB RAM and a 400 MB hard disc. Data are stored in 24-bit words. Two analogue–digital converters (ADCs) are integrated for transient recording. A fast ADC with 20 MHz sampling rate and 9-bit resolution is used for broadband detection, and a slow ADC with 50 kHz sampling rate and 12 bit resolution is used for high-resolution heterodyne detection. The lowest detectable mass, i.e. the highest detectable frequency, is limited by the sampling rate of the fast ADC to 11.5 amu. Transients up to 128 kwords can be recorded. A fast Fourier transform processor undertakes the computationally demanding Fourier transformation of the transient. It is fast enough to allow for an online display of a non-linearized mass spectrum for transients up to 32 kwords, which is used for signal optimization.

The I89 FT-ICR operating system allows software control of the experiment by automated routines. Up to 10 different pulses can be applied for a variety of purposes, such as ion excitation, gating of the ion trap or triggering of external hardware, e.g. lasers or pulsed valves. The pulse lengths may be integer multiples of 1 μs, the delays between pulses are integer multiples of 10 μs. Combining pulses and delays, real-time control with an overall resolution of 1 μs is achieved.

The mass spectra are transferred using a Bruker software package (NMRLINK) to an external personal computer, which is then linked to the local UNIX workstation cluster. In addition, the mass intensity information can be transferred from the ASPECT to the PC in ASCII format via an RS232 serial port and further processed under UNIX, to enable, for example, fitting of the reaction kinetics.

2.2. *The laser vaporization molecular beam ion source*

Most of the experiments use a versatile cluster beam source developed in our laboratory [66], combining laser vaporization in the presence of a high gas pressure with supersonic expansion [66–68], illustrated in figure 2. Ablation of the metal, usually in the form of a rotating disc target, is achieved by a 5 ns pulse of a frequency-doubled Nd:YAG laser (Continuum Surelite II), with a typical energy

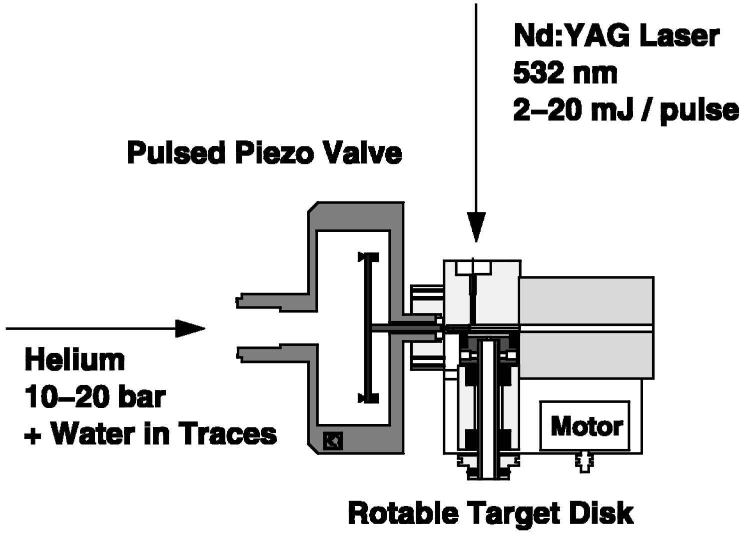

Figure 2. Laser vaporization molecular beam ion source. Material is vaporized with a 5 ns laser pulse from a rotating target disc (YAG, yttrium aluminium garnet). Together with an accurately timed, ~50 μs short gas pulse, the hot plasma is expanded via a confining channel into high vacuum. The plasma is collisionally cooled, and clusters are formed in the supersonic expansion. Hydrated ions are produced by adding traces of water to the carrier gas. Reproduced with permission from reference [58]. © 1995 American Institute of Physics.

of 2–20 mJ. The source yields ions without the need for post-ionization. The plasma is entrained into a precisely timed pulse of a carrier gas, usually helium, and cooled by supersonic expansion into the high vacuum of the source chamber. Depending on the polarity of the electrostatic ion transfer optics, either cations or anions can be extracted from the source [69]. By seeding the carrier gas with water vapour, metal ions solvated by up to 100 molecules of water or any other solvent can be produced [12, 30].

The pulse of the carrier gas is supplied by a home-built piezoelectric valve [58, 60] which is the outcome of an in-house development that goes back to an initial design by Proch and Trickl [70]. It is driven by a pulse from a home-designed pulsing circuit, typically 50 μs long, up to 1 kV amplitude. The proper delays of the laser pulse and gas pulse and their integration into the ICR duty cycle are obtained with the help of a control program, with the pulse sequence and timing of a typical experiment shown schematically in figure 3. Each data acquisition cycle starts with a quench pulse P1, which cleans the ICR cell of ions that might be left trapped from the previous cycle. Subsequently the cell is filled by accumulating the ions over typically 20 cycles of ion generation and trapping, each of them consisting of firing of the flash lamps, opening the piezoelectric valve and activating the laser Q-switch trigger.

A so-called gate pulse P2 lowers the trapping voltage of the first trapping plate to 0 V, allowing the ions to enter the ICR cell. By changing the delay D5 and shifting P2, one can utilize time-of-flight effects to preselect crudely ions of certain masses and stoichiometry. The amounts of ions produced, as well as their composition, are critically dependent on the relative timing between the gas pulse and the laser pulse. In particular, in the case of the hydrated metal ions, this timing has to be accurate to

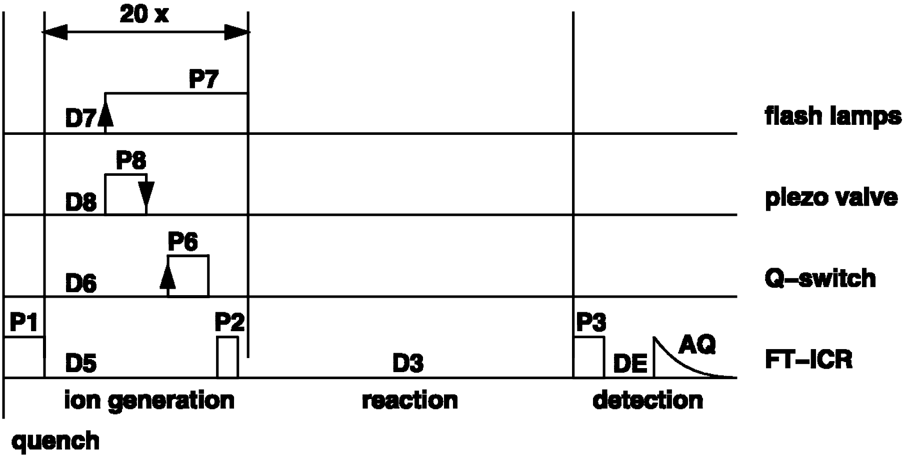

Figure 3. Pulse sequence of a typical ICR experiment with the laser vaporization source. The quench pulse P1 ejects all charged particles from the cell, which is subsequently filled in typically 20 ion generation cycles. The piezo valve is triggered with the falling edge of the pulse, which allows 1 μs accuracy. After a reaction delay, the ions in the cell are accerlerated by the broadband pulse P3 and the transient recorded during AQ. The short delay DE ensures that the transient is not affected by the pulse P3.

1 μs to ensure a maximum yield of the desired species. Ion generation and accumulation in the cell may be followed by an optional mass selection, and then by a variable reaction delay, allowing a reaction or other processes to occur prior to the detection of the ions and recording of the mass spectrum.

3. Water clusters and their black-body radiation induced fragmentation

As described above, our versatile laser vaporization source makes it possible to generate cationic or anionic aggregates of the type $X^{\pm}(H_2O)_n$, with n up to about 170, and where X can be just about any atom, atom cluster or small molecule. While the source usually produces clusters with a distribution of different n values, owing to the ability of the FT-ICR method to eject unwanted species, the clusters can be individually mass selected if so desired. They provide a medium where various aqueous or other solution reactions can be studied.

In spite of the essentially collision-free environment of the ICR cell, the trapped clusters do not survive there indefinitely, since they gradually absorb the black-body infrared radiation from the apparatus walls and fragment by losing individual solvent molecules [11, 30, 71–74]. As we have shown in a number of our previous studies, regardless of the central ion, the fragmentation rate due to this process is roughly proportional to the number of ligands n [11, 17, 19, 21, 30–32, 34], and this effectively places an upper limit on the maximum size of clusters which can be investigated in our apparatus. Figure 4 shows the largest protonated water clusters that we have been able to obtain so far, with a distribution $H(H_2O)_n^+$ ranging from $n = 45$ to 170. The spectrum illustrates both the power and the limitations of our current setup. At room temperature, the lifetime of an $n = 50$ cluster amounts to 0.10 s; at $n = 170$ it goes down to 0.030 s. At the same time, the aquisition period, i.e. the transient recording time, is 0.090 s for the chosen mass range and data set size. If the lifetime of an ion is of the order of the acquisition time or less, significant lifetime

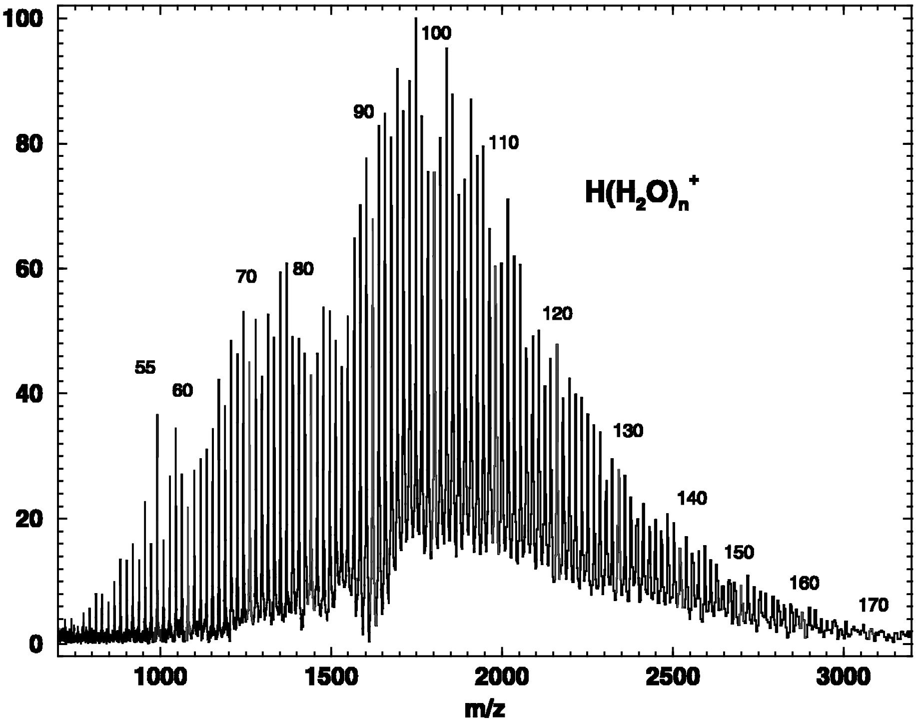

Figure 4. Mass spectrum of very large $H(H_2O)_n^+$ protonated water cluster produced in the laser vaporization source with an aluminium target and a high laser pulse energy. The extreme increase of the noise level beyond $n \approx 70$ is due to the reduced lifetime of the clusters. When the lifetime becomes smaller than the acquisition time, in this case 0.090 s, the peaks broaden and resolution is lost. This limits the upper cluster size which can be reasonably studied with our current data station.

broadening is observed, and the bases of the peaks start to overlap. The low signal-to-noise ratio starting around $n = 70$ illustrates this effect. Based on this argument, one may speculate on the existence of a stability island around $n = 90$, i.e. clusters with $n = 88$–92 may have a signicantly longer lifetime than their neighbours, since the noise level is significantly lowered in this regime. The spectrum also illustrates that, because of the limited resolution for larger clusters, reactivity studies are feasible only for $n \lesssim 70$, which is the range covered by most of our studies.

Obviously, the rate of black-body fragmentation is a function of the wall temperature, since the energy radiated by a black body is proportional to T^4. Clearly, cooling the cell walls could drastically reduce the rate of fragmentation and extend the range of cluster sizes which could be investigated.

While on one hand being a limitation in terms of restricting the size of clusters which can be studied, on the other hand the black-body fragmentation is an extremely important tool in many of our solvation studies. As the clusters gradually absorb energy from the walls, one can in a controlled way evaporate the ligands one by one, and in this way observe and investigate in detail the effect of the removal of the stabilizing solvent on the cluster chemistry.

By introducing a reaction gas at a controlled pressure into the ICR cell, typically in the 10^{-8}–10^{-9} mbar range, the stored clusters can be made to collide with the desired gaseous reactants. In the course of such a collision, the gas molecule or atom can react with one of the molecules on the cluster surface, it can be exchanged for one of the existing ligands or it can be 'dissolved' within the cluster. The extremely high resolution of the FT-ICR mass spectrometer has the advantage that the exact elemental composition of the individual clusters as well as of their reaction products can be accurately determined, and from this information the detailed nature of the reactions occurring in the cluster can often be unambiguously inferred.

As will be discussed more in the following section, the above method of introducing reactants into the cluster in gas phase collisions works extremely well with species capable of hydrogen bonding with the aqueous cluster surface, for instance ammonia [36], HCl or HBr [7, 8, 17, 19, 21, 27, 31, 33], or even with strongly polar species, for instance carbonyl compounds [16] or ethers [9]. The primary step of such a 'dissolution' reaction is usually in principle a ligand exchange, where the desired reactant replaces one or several of the existing water ligands in the cluster. In essence, the technique works well as long as the reactant molecule is bound to the aqueous cluster more strongly than, or at least with comparable strength to, the water ligands. The method usually fails with highly volatile molecules, which are bound to the cluster surface much more weakly than the water ligands. For example, when species such as CO_2, N_2, O_2 or even CO are introduced into the cell, one only observes an enhanced collisional fragmentation and an accelerated loss of the solvent ligands, but usually no evidence of their incorporation into the droplets or of their chemical reaction with the ionic core.

Introduction of such species should in principle be possible by simply adding them to the carrier gas and incorporating them into the cluster directly in the supersonic expansion. We have recently demonstrated that one can 'soft land' such weakly bound, non-polar species on metal clusters by exchanging them for even more weakly bound ligands, such as argon or xenon [13, 26]. Thus it should be feasible first to produce mixed clusters of the type, for instance, $X^{\pm}(H_2O)_nAr_m$, and then in the ICR cell to exchange collisionally the non-polar reactant for the argon atoms. Such an approach, however, considerably increases the complexity of the entire experiment and has the disadvantage that the nanodroplets are produced significantly colder. This may reduce the probability of the molecule introduced in this way penetrating the aqueous solvent shell and interacting with the ionic core. Furthermore, as the clusters warm up owing to black-body infrared absorption, chances are that the molecules introduced by such ligand exchange will again 'evaporate' from the aggregate, before a chemical reaction may take place.

In the following sections, we will look in some more detail at the various types of solution-like chemistry and processes investigated in water clusters.

4. Solution phase chemistry in clusters

4.1. *Ionic dissociation in water clusters*

It is instructive to examine the 'solubility' of molecules such as HCl or HBr in water clusters in more detail. When one examines this process as a function of cluster size, one finds that these species can be incorporated into the $H^+(H_2O)_n$ clusters only for $n > 10$ [7, 75], and, conversely, when in the course of fragmentation of larger clusters the number of solvent molecules reaches this limit, the hydrogen halide molecule, rather than another water ligand, will evaporate from the cluster. The explanation is simple: since hydrogen halides dissolve with ionization, three ions, that is two protons and the negatively charged halide anion, have to be stabilized in the cluster, and this apparently requires approximately 10 water molecules. When the required number of solvent molecules is no longer available, the halide anion recombines with one of the protons, and the covalent hydrogen halide, being more weakly bound to the cluster than the water ligands, evaporates from its surface.

It is now well established by theory [76–81] that four water molecules are needed to dissociate HCl ionically in the gas phase, as indicated by earlier matrix isolation studies [82, 83]. Six water molecules dissolve a single NaCl unit [152]. Stabilization of an additional charge such as a proton obviously needs considerably more water molecules, possibly because Coulomb repulsion requires a fairly remote arrangement of the charge carriers with the same polarity.

Of interest is also the 'neutralization' reaction of hydrogen chloride or a similar acid with clusters of the type $M^+(H_2O)_n$ which contain a metal cation of a basic hydroxide such as Na^+ [27, 84] instead of H^+. Actually, the exothermic part of a bulk acid–base neutralization reaction is really the H^+–OH^- recombination, so that dissolution of the acid in the hydrated metal cation cluster is not much different from that in hydrated proton clusters, since no OH^- ion is present for recombination. The exchange of the acid, e.g. HCl, for a water ligand is followed by its ionic dissociation, so that the product cluster again contains three separate, hydrated ions, that is H^+, Cl^- and the metal cation M^+. Besides the ionic dissociation and fragmentation no true chemical reaction takes place. Again, a minimum of 10–12 water ligands is required for the HCl to dissolve, and no reaction other than fragmentation is observed for smaller clusters. Conversely, when a larger cluster is allowed to fragment gradually and to evaporate ligands; when this limit is reached the H^+ and Cl^- ions recombine again, and the HCl evaporates from its surface.

4.2. *Reduction-oxidation reactions*

4.2.1. *Metal oxidation and hydrogen formation*

As noted previously, the laser vaporization technique employed in our experiments produces predominantly singly ionized metal cations in the water cluster. An interesting situation arises when the +I oxidation state is unusual for the metal in question, as for example in the case of magnesium, which normally occurs in the form of hydrated Mg^{2+} ions, or aluminium, which exhibits a strong preference for the Al^{3+} oxidation state. In spite of that, a metal in an unusual oxidation state can be prepared in the cluster [12, 14, 19, 21, 33–35] and studied on the time scale of the many seconds FT-ICR experiment. One finds, however, that while in certain cluster size ranges the monovalent ions appear stable and are able to survive for a long time, in other ranges of n values a spontaneous oxidation of the metal, with a simultaneous reduction of water and formation of atomic or molecular hydrogen, takes place. Thus the clusters with $Al^+(H_2O)_n$ composition appear stable, as long as $n \geq 24$ [12, 21, 35]. As such clusters absorb the black-body photons, they simply lose water ligands on a 100 ms time scale. When, however, the critical $n = 23$ limit is reached, a new reaction channel, in competition with the unimolecular fragmentation, opens up. The metal is oxidized to Al^{3+}, simultaneously reducing water with the evolution of molecular hydrogen:

$$Al^+(H_2O)_n + h\nu \rightarrow Al(OH)_2^+(H_2O)_{n-x-2} + H_2 + xH_2O, x = 2, 3. \qquad (1)$$

The heat released by this exothermic reaction leads also to the evaporation of two or three water ligands. Interestingly, this redox reaction channel closes again when

$n \prec 12$. Smaller $Al^+(H_2O)_n$ clusters just fragment, without aluminium being oxidized. Similar observations were made for magnesium, where the magnesium is oxidized to Mg^{2+}, but in this case free hydrogen atoms, H, are formed [14, 19]:

$$Mg^+(H_2O)_n + h\nu \rightarrow MgOH^+(H_2O)_{n-y-1} + H + yH_2O, y = 1, 2. \quad (2)$$

This reaction again occurs only within a relatively narrow range of cluster sizes, for $n = 16$–21. However, for $n = 5$–15 the reaction seems to be so efficient that the $Mg^+(H_2O)_n$ precursor is not observed at all.

Still a different case is represented by some transition metals which can occur in solutions in several oxidation states. Vanadium, for example, is known to form hexahydrate ions $V^{2+}(H_2O)_6$ as well as $V^{3+}(H_2O)_6$ that are stable in solution. Here again, monovalent ions $V^+(H_2O)_n$ are stable as long as $n \geq 24$, but, for smaller n values, redox reactions analogous to either reaction (1) or reaction (2) are observed [34]. Most of the smaller clusters exhibit reaction (1), with $x = 3$, that is accompanied by evaporation of three water ligands, but with the $n = 9$–12 clusters also showing reaction (2), but with $y = 0$ or 1. Because of the lower exothermicity or even slight endothermicity of the latter reaction, at most one water ligand can evaporate. Interestingly, the $n = 15$ cluster specifically exhibits no redox reaction, and also all $n \prec 8$ species only fragment unimolecularly.

The fact that most of these intracluster reduction–oxidation reactions are accompanied, in addition to hydrogen loss, also by the evaporation of several (typically two or three) water molecules indicates that their exothermicity must be of the order of twice the water sublimation enthalpy, somewhere around $100\,\mathrm{kJ\,mol^{-1}}$. This shows that the fact that the reaction is not detected in some of the clusters, and in particular that it does not occur in clusters above a certain size limit, is not due to the thermochemistry of the process but rather to a high activation barrier. Possibly when the number of ligands drops below a certain limit, the solvation shell around the central ion is destabilized, and the barrier height reduced so that the redox reaction can take place. Another explanation, however, could involve entropic effects [32], discussed in more detail in a later section.

4.2.2. *Proton-catalysed metal oxidation*

Interestingly, the redox reactions discussed above can, even in the large clusters where they do not occur spontaneously, be immediately triggered or 'acid catalysed' by dissolving a molecule of an acid, such as HCl, in the cluster. Thus a bimolecular reaction of $Mg^+(H_2O)_n$ clusters with HCl results in the release of an H atom and formation of $MgCl^+(H_2O)_{n-x}$ [19], even if n is well outside the range where the oxidation is observed to occur spontaneously. A similar reaction also occurs in aluminium clusters, where an Al^{3+} chloride–hydroxide forms in the first step [21]:

$$Al^+(H_2O)_n + HCl \rightarrow AlOHCl^+(H_2O)_{n-1-x} + H_2 + xH_2O. \quad (3)$$

This can then in subsequent steps react with further HCl molecules, resulting in hydrated aluminium chloride species, $AlCl_2{}^+(H_2O)_n$.

It is interesting to note, however, that all the above reactions with HCl or other acids again take only place when more than about 11 water ligands are present. This indicates that the first step of these reactions is ionic dissolution of the hydrochloric acid in the water cluster. In the absence of sufficient solvent for the HCl to dissolve, ionic dissociation cannot occur, and the presumably proton-catalysed intracluster metal oxidation cannot take place.

Quite intriguing in this context is the existence of a lower limit of about $n = 11$ for the spontaneous aluminium oxidation [12, 21]. We have previously suggested that this is due to a concerted process, in which a proton is transferred to a first solvation shell water molecule [12, 21, 35]. We have proposed that, for this proton transfer, leading then to the transfer of an electron with neutralization of H_3O^+ and formation of a hydrogen atom or molecule, a chain of at least two outer-shell water molecules linking two first-shell ligands is required. The fact that outside the range where the reaction spontaneously occurs it can be promoted or driven by dissolving acid in the cluster provides strong support for the proton transfer mechanism [21, 35].

A seemingly completely different reaction, conversion of SO_3 to H_2SO_4 in the presence of water, is now, owing to its relevance for atmospheric chemistry, exceedingly well studied. As early as 1985, matrix isolation studies of SO_3–$(H_2O)_n$, $n = 1, 2$, complexes [85] indicated that the second water molecule is needed actually to form a molecule of sulphuric acid, while one water molecule leads to formation of an $SO_3 \cdot H_2O$ complex. Almost 10 years of experimental [86, 87] and theoretical [88, 89] studies focusing on the $SO_3 + H_2O$ reaction had to elapse until the mechanism involving the second water molecule was identified [90, 91]. It is now well established [92–97] that the second water molecule lowers the geometric constraints, thus enabling a low-energy pathway for a concerted proton transfer leading to H_2SO_4 formation.

In a number of theoretical works by several different authors it was recently found that concerted proton transfers through a water chain can significantly reduce the activation energy of a reaction [98–103]. Siegbahn modelled the Wacker process with two, three and four water molecule chains [98]. Nguyen *et al.* studied the hydration of carbon dioxide with similar models [99]. Molecular dynamics studies of the methyl chloride hydrolysis were undertaken with explicit consideration of three water molecules by Aida *et al.* [100], and Yamataka and Aida undertook molecular orbital calculations up to the MP2/6-31+G* level of theory with up to 13 water molecules [101, 102]. Up to four water molecules were used in the B3LYP/6-31G** calculations of the chlorination of ammonia by hypochlorous acid by Andrés *et al.* [103]. In each case, the concerted proton transfer through a chain of typically three water molecules lowers the activation energy for the process to a level which is comparable with solution phase chemistry. Thirteen water molecules have been enough to reproduce the experimental energetics and various deuterium kinetic isotope effects in the methyl chloride hydrolysis [101, 102]. Perhaps the well-known activation of CH bonds and an efficient isotopic exchange in various organic compounds in a strongly acidic medium could also be mentioned in this context. Coming back to the title question, two to four water molecules in the right place can apparently provide a low-energy pathway for a proton transfer, and a theoretical model of 13 water molecules seems large enough to even account for kinetic isotope effects.

4.3. *Insoluble salt precipitation*

4.3.1. *Single-molecule precipitation of AgCl*

As we discussed above, when clusters containing dissolved hydrochloric acid gradually fragment, as soon as a certain minimum number of water ligands required to stabilize the ionically dissociated acid is reached, the ions recombine, and the volatile hydrogen halide, rather than a water molecule, is lost. This occurs close to

$n = 11$, regardless of whether the central ion is a proton [7] or a monovalent metal such as Na^+ or K^+ [27, 84]. On the other hand, when the same experiment is performed with clusters containing Ag^+, this loss of the last HCl molecule only takes place for $n = 4$ [27]. The difference between the two cases is that NaCl and KCl are very soluble in water, but silver chloride is one of the least soluble compounds. While the former chloride is ionically dissociated, as soon as HCl is introduced into a cluster containing silver, the Ag^+ and Cl^- ions 'precipitate' from the solution as an insoluble AgCl molecule. In view of this, only a few water molecules are needed to stabilize the H^+, the only ion remaining in the cluster.

Obviously, the ionization potential of a free hydrogen atom (13.595 eV) is much larger than that of a silver atom (7.57 eV) or of silver chloride. In aqueous solution, the H atom ionization potential is lowered drastically, much more so than those of any other ions, and the situation is reversed. The stabilization of the proton, however, is progressively reduced with the decreasing number of water ligands. Apparently, when their number is reduced to around $n = 4$, a charge transfer takes place within the cluster. While to understand the exact course of the reaction would require a detailed quantum chemical computation, the covalent AgCl is probably attacked by the almost bare proton, which induces the formation of an Ag^+–Cl^- ion pair state [52, 104, 105]. The proton can now recombine with Cl^-, yielding a hydrogen chloride molecule, which evaporates from the cluster.

In a similar experiment with hydrogen bromide instead of hydrogen chloride, the silver bromide single-molecule precipitate AgBr is formed. In a bulk solution, AgBr is even less soluble than the chloride, and the last hydrogen bromide molecule is observed to evaporate only when $n = 3$, that is when only three water ligands remain in the cluster [106]. The minimum value of n at which the hydrogen halide is lost can therefore in a way be viewed as a measure of the solubility of the metal salt.

4.3.2. *Solubilities of transition metal(I) halides*

In one of the previous sections we have noted that, using laser vaporization, one invariably produces ions in the +I oxidation state, irrespective of the preferred valence states of the metal [12, 14, 19, 21, 35]. These then exhibit an appreciable stability and may survive for the many-second duration of the FT-ICR experiment. We have, however also discussed how the ions produced in this way in an unusual valence state may undergo an intracluster reaction, when in the course of the fragmentation process the stability of the solvation shell is reduced. They then reduce one or more of the water ligand molecules with the development of hydrogen, while the metal is oxidized to its favoured oxidation state. A characteristic property of transition metals, with their open d electron shell, is their ability to form stable compounds in a variety of different oxidation states. Typically, however, in view of their usual s^2 valence shell electron configuration, they rarely occur as monovalent ions in solutions. One might therefore expect that, similarly to magnesium or aluminium, the hydrated M^+ ions of transition metals will be oxidized to one of the higher, more favourable oxidation states.

We have therefore investigated the first-row transition metals Ti, V, Cr, Mn, Fe, Co, Ni and Cu. Except titanium, for which only hydroxide cations were observed, for all the other metals we were able to generate solvated ion clusters $M^+(H_2O)_n$, with sizes ranging up to $n > 50$. Among these, however, only vanadium, as discussed above, undergoes a redox reaction, resulting depending on the size of the hydration shell in either V^{3+} or V^{2+} [34]. All the other metals only gradually fragment but

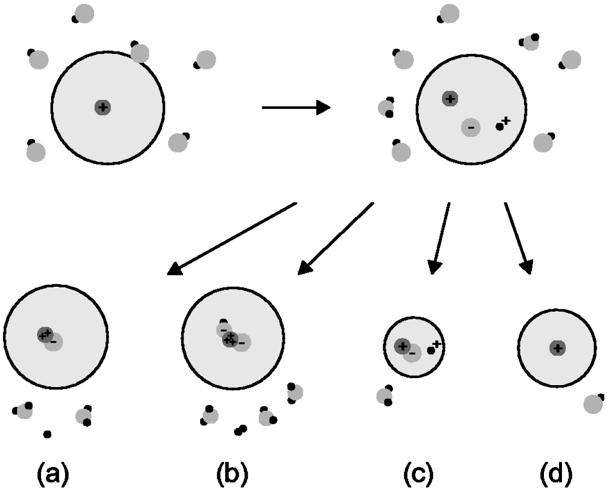

Figure 5. Possible reaction pathways of hydrated metal(I) cations with HCl. In a reactive collision with HCl, the molecule is ionically dissolved in the cluster, and typically two water molecules are released owing to the reaction enthalpy. (*a*) The metal ion is oxidized to +II, thereby reducing the proton to atomic hydrogen, which is eliminated together with typically two water molecules. (*b*) If the preferred oxidation state of the metal is +III, the proton and a hydrogen atom in a water molecule are both reduced, releasing molecular hydrogen and typically three water molecules from the cluster. (*c*) No redox reaction takes place when a single molecule of M(I)Cl precipitates in the strongly acidic water cluster with pH $\prec 0$. Water molecules are gradually lost until the cluster becomes very small. (*d*) If no precipitation or redox reaction takes place, three individual ions need to be solvated by water. Solvation breaks down at fairly large sizes of the cluster, and a molecule of HCl is released. Reproduced with permission from reference [33]. © 2002 American Chemical Society.

remain in the +I oxidation state. Based on the experience with the main group metals, one might expect that dissolving, for example, hydrogen chloride in the cluster might again 'catalyse' the oxidation of the M^+ cation. Quite surprisingly, however, although HCl can again be dissolved in the larger clusters, no oxidation is observed [33].

The clusters containing the chloride gradually lose, on a millisecond time scale, the water ligands owing to both collisions and to the absorption of black-body radiation. The loss of the last HCl molecule then occurs not around $n = 11$–12, as in clusters containing soluble species such as NaCl or HCl, but, depending on the metal, between $n = 3$ and $n = 7$, similar to the clusters containing 'insoluble' AgCl or AgBr. A logical interpretation of this result is that the otherwise unknown metal +I chlorides of these transition metals are highly insoluble and like silver chloride or bromide are present in the clusters as MCl single-molecule precipitates. The extremely rapid 'precipitation', that is formation of the insoluble chloride molecule, then shields the metal cation from being oxidized.

Coming back to the title question, the presented results suggest that dissolution and precipitation phenomena can be studied in a cluster size region of $n = 3$–15 water molecules, in combination with stepwise dehydration, as summarized in figure 5. Although around 11 water molecules are sufficient to prevent HCl loss from the cluster, two or three more are needed actually to stabilize the incoming solute, since some water molecules are lost in the initial ligand exchange. On stepwise dehydration, the HCl molecule is lost at a certain n, and this n appears to correlate with the solubility of the metal chloride.

4.4. *Base-catalysed aldol condensation*

Numerous reactions, both organic and inorganic, proceed much more efficiently in strongly acidic or strongly basic solutions than in neutral ones. In fact, one of the earliest catalytic reactions observed, the hydrolysis of starch into glucose reported first at the turn of 18th century by Kirchhoff, is an example of such an acid-catalysed process. The fundamental principle of such base- or acid-catalysed reactions is easy to understand. The ions – either H^+ or OH^- – present in the solution are attached to one of the reacting molecules, and in this way a neutral–neutral interaction is converted to a much faster and more efficient ion–neutral reaction. One can note that a 'hydrated proton' gas phase cluster $H^+(H_2O)_{55}$ has about the same proton concentration as a strong acid with $pH \approx 0$ and, conversely, an $OH^-(H_2O)_{55}$ cluster resembles a strongly basic $pH \approx 14$ solution, and one might wonder whether they will chemically behave as such.

An example of a well-known base-catalysed reaction is the so-called 'aldol condensation', in some sense the reverse of the early Kirchhoff reaction. We have examined large ionic water clusters in which aldehydes or ketones were dissolved [16]. The experiments have shown that both acetaldehyde and acetone can easily be 'dissolved' in the ionic water clusters, with the carbonyl compounds being efficiently exchanged for the water ligands. When this ligand exchange and concurrent fragmentation are carried to completion, in the case of the $H^+(H_2O)_n$ ions the final product is simply a proton solvated by two acetaldehyde or acetone molecules.

When, on the other hand, the 'basic' $OH^-(H_2O)_n$ clusters are so investigated, one obtains with acetaldehyde as the final product an ion of mass 87, corresponding to the composition $CH_3CHO^-CH_2CHO$. This is an aldolate anion, formed by condensation of two acetaldehyde molecules, with the loss of one hydrogen atom, and the formation of a new covalent C–C bond. Experiments with selectively deuterated reactants then show unambiguously that the hydrogen is lost from the methyl group of the acetaldehyde, rather than from its aldehydic group. As in bulk solutions, the aldol condensation is efficiently catalysed by bases, i.e. by OH^- anions. Clearly, the clusters containing the hydroxyl anions behave like strongly basic bulk solutions.

The presence of the 'uncondensed' acetaldehyde–water cluster $(CH_3CHO)_2OH^-$ after very long reaction times indicates again that a minimum cluster size is required for the aldol addition reaction to occur. Because of a number of competing effects, the exact lower size limit could in this case not be determined. However, from the relative abundance of the products and the initial size distribution of the $OH^-(H_2O)_n$ clusters one can infer that $n = 5$ is probably not enough, while $n = 15$ will definitely enable the reaction. Again, around $n \approx 10$ water molecules, albeit with a relatively large error, make a solution.

4.5. *Hydrolysis of chlorine nitrate on a cluster surface*

Chlorine nitrate is an important species in the stratospheric ozone chemistry. It is now well understood that chlorine atoms catalyse very efficiently the ozone destruction cycle [107–115]. Over time, however, chlorine is removed from the catalytic cycle owing to the formation of so-called 'reservoir compounds', mainly hydrochloric acid and chlorine nitrate, $ClONO_2$, which are relatively stable and do not directly participate in the catalysis. During the polar winter when the temperature of the stratosphere drops to between −80 and −85°C, however, the so-called polar stratospheric clouds (PSCs) form [115–117]. It is believed that heterogeneous reactions on their surface hydrolyse and destroy the reservoir compounds [114], which are eventually, during the polar spring, reintroduced in more active forms back into the catalytic cycle and are responsible for the enhanced seasonal ozone depletion and the formation of the 'ozone hole'.

The PSCs are basically micron-size particles consisting of water, nitric acid and other impurities. We have therefore suggested that the microscopic ionic clusters produced in our ICR studies could be used as models for these reactions and investigated the reactions of chlorine nitrate with both positively and negatively charged water clusters [10]. Our studies have shown that both anionic and cationic clusters react with chlorine nitrate, with the former reacting with almost collisional rates and the latter about an order of magnitude more slowly. In either case, the chlorine nitrate is hydrolysed, with the nitrate incorporated into the cluster and the chlorine being returned into the gas phase in the form of hypochlorous acid, HOCl:

$$H^+(H_2O)_n + ClONO_2 \rightarrow H^+(H_2O)_{n-x}(HNO_3) + HOCl + xH_2O, \qquad (4)$$

$$OH^-(H_2O)_n + ClONO_2 \rightarrow NO_3^-(H_2O)_{n-x} + HOCl + xH_2O. \qquad (5)$$

The labile hypochlorous acid would, of course, be readily photolysed in the stratosphere, returning the chlorine to the chemical cycle. It is interesting to note that, in the case of the anion, an exchange of the OH^- ionic core for nitrate takes place. During further fragmentation of the cationic clusters, when the number of ligands drops below about $n = 4$, there is also a switch in the ionic core, $H^+(H_2O)_m(HNO_3) \leftrightarrow NO_2^+(H_2O)_{m+1}$, with a nitronium cation becoming the charge carrier [118, 119].

In a recent study by Gilligan and Castleman [120], a clear absence of reactivity is shown for $D^+(D_2O)_n$ clusters with $ClONO_2$, albeit with $n \lesssim 12$. In our study, considerably larger $H^+(H_2O)_n$ clusters, $n = 8$–26, were present, and the mass spectrum after 5 s reveals that smaller clusters decay exclusively by fragmentation, without exhibiting any reactions. Again, the cluster has to be large enough to dissolve ionically a $ClONO_2$ molecule, in order to undergo the aforementioned reaction, with a minimum size of $n \approx 10$–12. Instead of being contradictory, our earlier results are in perfect agreement with the recent study by Gilligan and Castleman [120, 121], and the absence of reactivity in their study is probably due to the limited cluster size range.

4.6. *Acid hydrolysis and ICl formation in $I(H_2O)_n^+$*

Cationic water clusters containing iodine, of the somewhat unexpected composition $I(H_2O)_n^+$, $n = 0$–25, can be easily generated in a laser vaporization source when a pressed NaI disc is used as the target material [31]. Density functional calculations illustrate the conceptual differences between the cationic and anionic iodine–water clusters $I(H_2O)_n^\pm$. While $I^-(H_2O)_n$ is genuinely a hydrated iodide ion, the cationic closed-shell species $I(H_2O)_n^+$ may be best viewed as a protonated water cluster, in which one water molecule is replaced by hypoiodous acid (figure 6). In the strongly acidic environment, HOI is protonated because of its high proton affinity. However, similarly to the well-known $H_3O^+/H_5O_2^+$, Eigen ion vs. Zundel ion controversy for aqueous solutions [39, 122], a smooth transition between H_2IO^+ and $H_4IO_2^+$ as core

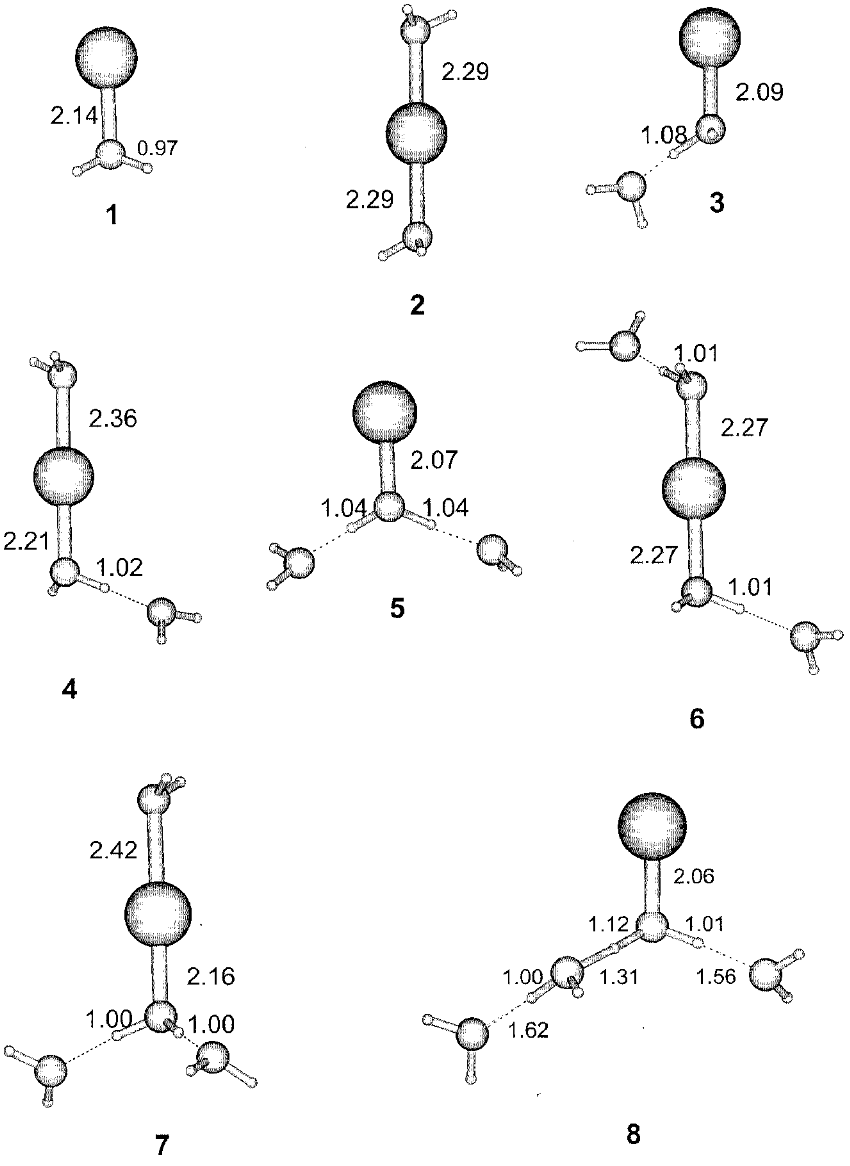

Figure 6. Fully optimized structures of $I(H_2O)_n^+$, $n = 1$–4, at the B3LYP level of theory. Bond lengths are in ångstroms. All O–H bonds except where otherwise noted are 0.97 Å. A smooth transition from H_2OI^+ to $H_4O_2I^+$ as core ion is observed, and, with increasing asymmetric solvation, proton-bound structures emerge, as evidenced in structure **8**. Reproduced with permission from reference [31]. © 2001 American Chemical Society.

ions is observed for different cluster sizes. While $H_4IO_2^+$ is bridged by the iodine, proton-bound structures may develop with an increasing number of water ligands and with asymmetric solvation.

Again, chemical reactions with hydrochloric acid were investigated. While smaller cationic iodine–water clusters $I(H_2O)_n^+$, $n \lesssim 10$, only fragment and lose the water ligands, the larger species with $n \gtrsim 11$ react chemically, releasing the ICl interhalogen and resulting in hydrated proton clusters. Obviously, HCl is ionically dissolved in the cluster and, almost immediately, an HOI molecule is hydrolysed, and Cl^- recombines with the formal I^+ to ICl. This reaction is well known as acid hydrolysis from bulk solution, and the equilibrium in fact lies on the side of the interhalogen in strongly acidic solutions. As soon as the cluster is large enough to dissolve HCl ionically, the reaction can proceed. Little more than 10 water molecules are again sufficient for this solution phase reaction to occur in the cluster.

4.7. *Stabilization of a proton in aqueous clusters*

In many respects the proton is the most important ion, and its solvation is of utmost importance in solution chemistry. Solvation of ions is naturally governed by electrostatic, Coulombic interactions, whose strength depends crucially on the distance between the charges and hence on the size of the ions. The proton, since it has no electrons, is unique, as from the chemical point of view it is just a dimensionless point charge and will therefore form the strongest bonds. Using a simple electrostatic model it is easy to show that the proton also differs from almost all other ions—with a few exceptions—in that it strongly prefers to be coordinated to two and only two ligands [22]. The proton and its solvation have a great influence on solution chemistry, and they can be very easily studied in finite clusters.

The hydrogen atom has an ionization potential higher than most other elements or simple compounds, and in particular than metals, but in view of the extremely stable solvation shell the situation is reversed in aqueous solution, and this situation is clearly reflected in solution chemistry, as can be seen in a number of reactions presented in this article. A classical example is the behaviour of the insoluble salt precipitates formed by dissolving hydrochloric acid in solvated metal cation clusters such as $Ag^+(H_2O)_n$ [27]. As long as enough solvent was available, the solvated proton coexists in the cluster with the insoluble AgCl precipitate. When, however, the number of solvent molecules is no longer adequate to stabilize the proton, a charge transfer occurs and a hydrogen atom forms and then abstracts chlorine from the $AgCl^+$, with HCl evaporating from the cluster.

The extreme lowering of the hydrogen atom ionization energy by hydration is the basis of a number of ‘core switching’ cluster reactions, some of them of considerable importance in the atmosphere. The most abundant simple atmospheric ions O_2^+ and NO^+ are in regions where the pressure is sufficiently high for three-body collision to occur, leading eventually to solvate ion clusters of the type $O_2^+(H_2O)_n$, $n = 1$, 2, or $NO^+(H_2O)_n$, $n = 1$–3. As soon, however, as an additional ligand enters into the picture, a core switch takes place, resulting in a hydrated proton [123, 124]:

$$O_2^+(H_2O)_2 + H_2O \rightarrow H^+(H_2O)_2 + O_2 + OH, \tag{6}$$

$$NO^+(H_2O)_3 + H_2O \rightarrow H^+(H_2O)_2 + HNO_2. \tag{7}$$

A driving force behind this core switch is the ionization potential of the hydrogen atom, which becomes lower than that of O_2 or NO when at least two water ligands are present. The same effect is also responsible for the previously mentioned core switching reaction in clusters containing HNO_3, which have the structure of $H^+(H_2O)_n(HNO_3)$ for larger values of n but switch to $(NO_2^+)(H_2O)_{n+1}$ below about $n = 4$.

5. Upper size limit of electron detachment from $(H_2O)_n^-$: Entropic effects?

In our work on hydrated magnesium [14, 19] and aluminium [12, 21] ions, the intracluster reactions to form H and H_2, respectively, always compete with the loss of a single water ligand. Clusters bigger than a certain upper size limit decay exclusively by fragmentation, and no intracluster reaction can be observed. Recently, we studied the black-body radiation induced decay of hydrated electrons, $(H_2O)_n^-$ for $13 \prec n \prec 40$ and found a conceptually similar behaviour in the competition between electron detachment and water loss [32]. We found that while the larger clusters exclusively fragment, the importance of the detachment channel overall increases with decreasing size, but the trend is far from monotonic. Between $n = 14$ and $n = 30$ there appear to be large fluctuations and even–odd alternations in the relative importance of the two channels, as shown in figure 7. However, no electron

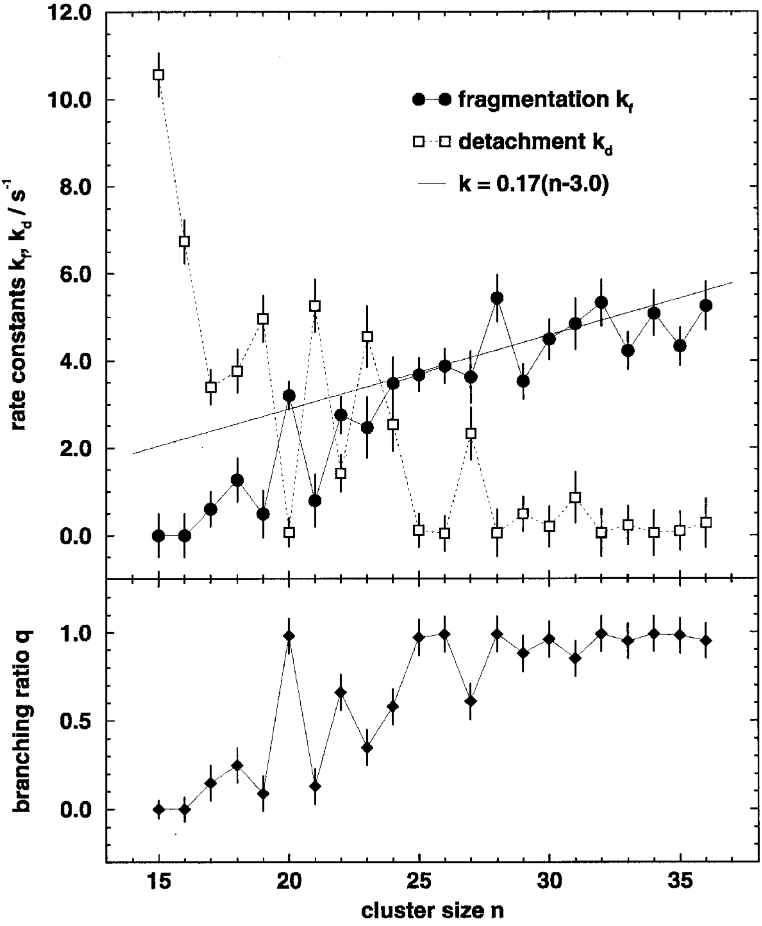

Figure 7. Partial rate constants k_f and k_d and branching ratio q of the black-body radiation induced decay of size-selected hydrated electrons $(H_2O)_n^-$ as functions of cluster size n. While the branching ratio q increases from 0 to 1 in going from $n = 17$ to $n = 32$, this increase is not monotonic, but shows a pronounced odd–even alternation around $n = 20$. Electron detachment leads to significantly increased total rate constants, which indicates that fluctuations in the detachment probability are the dominant source of the alternating branching ratio. Reproduced with permission from reference [32]. © 2001 American Institute of Physics.

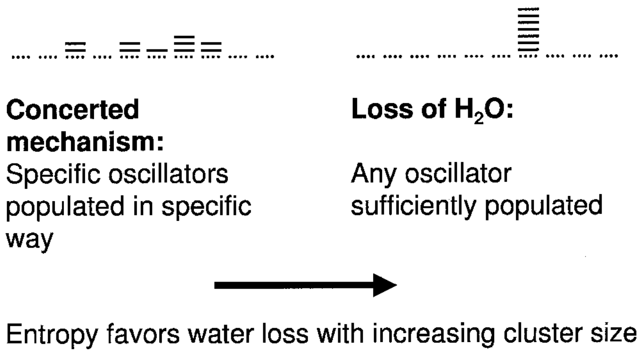

Figure 8. Illustration of entropic effects for the branching ratio of competing cluster reactions. Every reaction which requires a complicated pathway competes with the simple loss of a water molecule. In small clusters, the specific population of oscillators is relatively likely, while in larger clusters, with a vastly increasing number of possible populations, the sufficiently high population of any oscillator for fragmentation becomes dominant. This effect is probably enhanced by the fact that the complicated reaction requires a specific sequence of cluster rearrangements, which becomes less and less probable with cluster size, while any configuration can lose a water molecule, if any dissociative oscillator is sufficiently populated.

detachment was observed for any clusters larger than $n = 30$, and the branching ratio of the detachment channel overall levels off gradually.

Comparison of these results with spectroscopic data reveals that both the early photodetachment studies by Bowen and coworkers [125] and the more recent work by the Johnson group [126] find only a smooth, gradual variation in the absorption cross-section with cluster size, in the same region where we find numerous irregularities, and sharp oscillations. The major differences between the above optical spectroscopic studies and our mass spectrometric work are the time scale and the amount of energy available in the cluster. In our experiment, the clusters are gradually heated by the absorption of numerous far-infrared black-body photons on a time scale of 0.1–1 s, until enough energy is available to overcome the activation barrier, be it to electron detachment or loss of a water molecule. In the optical spectroscopy work, a single high-energy photon in the visible or near-infrared is absorbed by the cluster, heating it and raising its internal energy within femtoseconds. On the slow time scale of the FT ICR experiment there is enough time available to explore exhaustively the potential energy surface and to find a 'tight' transition state with the optimal reaction pathway and lowest activation barrier. Figure 8 tries to illustrate this in a very simplified manner. In reality, the situation is probably more complex, since a sequence of specific populations may be necessary for the complex reaction to occur. This then explains why minor, structure-dependent variations in activation barriers may result in pronounced, size-dependent fluctuations in the observed fragmentation rates and branching ratios. In the optical experiments, the decay proceeds fast, on the sub-s time scale of the molecular beam experiment. The heating with a single photon introduces sufficiently high energy excess into the cluster so that minor differences between different channels become irrelevant and pathways proceeding through the most 'probable', loose transition states will be favoured or vertical ionization into the continuum is accessible.

Also the upper size limit follows naturally from this argument: with increasing cluster size, more and more oscillators become available for dissociation, while more complicated rearrangements of water molecules which may be needed for the reaction to occur at a specific reaction site become less probable. Purely entropic effects could thus contribute to, or even be sufficient to explain, the upper size limit not only for electron detachment but also for hydrogen formation in hydrated metal ion clusters.

These arguments also reveal an interesting aspect of our title question. While the question suggests that a certain number of water molecules may be needed for a solution phase reaction to occur in the cluster, the upper size limits for the hydrogen elimination show that also a maximum number of water molecules in the cluster may exist for a given reaction to be observed. Since any chemical change competes with water loss, more complex reactions requiring moderate activation energies or temperature can be 'switched off' by making the cluster big enough. The bigger the cluster, the lower the temperature at which it fragments [11, 30]. As long as the fragmentation channel is significantly faster than the solution phase reaction, the latter will not be observed in the mass spectra of our experiment.

Recent calculations by Sobolewski and Domcke [127] reveal an interesting aspect of the hydrated electron problem. In the excited S_1 state of the water dimer, a hydrogen transfer takes place, resulting in two radicals, OH and H_3O. They argue that the hydrated hydronium could be responsible for the spectral signatures of the solvated electron in bulk water, a hypothesis which might prove to be most efficiently tested in the cluster.

6. Multiply charged hydrated ions

As an examination of any introductory book to inorganic chemistry will reveal, multiply charged ions in solutions are quite common, even though at first glance this might, in view of the high second and third ionization potentials of most metals compared with those of solvent molecules such as water, appear surprising. They owe their relative stability to the fact that the effect of the large ionization potentials is often compensated by the increasing solvation energies of small, multiply charged ions. In addition, the charge transfer from the metal to the water molecule leading to a Coulombic explosion requires the overcoming of a potential energy inherent in forming two separate positive charges, which may be quite significant [128–130]. As we have already mentioned, such multiply charged clusters are not produced by our existing laser vaporization source, which generates singly charged cations even for those metals which generally prefer higher states of ionization in solution. However, a number of elegant studies in other laboratories have shown that solvated, multiply charged cation clusters can be generated by several other methods, even though many of them can be shown to be metastable.

A generally useful technique for generation of multiply charged ions starting from bulk solutions is electrospray, and its applicability to doubly charged metal cations was clearly demonstrated in pioneering studies of Kebarle and coworkers [131–133] and by more recent studies in several other laboratories [56, 134]. Alternatively, the ions can be generated by first forming neutral clusters in supersonic expansions and then ionizing them by sufficiently energetic electrons, a technique employed by Stace *et al.* [135] and other groups. The formation of triply charged ions by these techniques with various solvents was also reported [136–138] but, so far, no triply charged hydrated ions have been observed in the gas phase.

Already the early studies by Fehsenfeld, Ferguson and coworkers had revealed a competition between charge transfer and complex formation [139, 140]. Quite recently, Stace *et al.* [135] speculated that, because of the high second ionization potential of copper, specifically the $Cu^{2+}(H_2O)$ complex should not be stable. In the course of the last year, however, the groups of Stone and Siu have succeeded in generating this 'elusive' ion by the collision-induced dissociation of larger $Cu^{2+}(H_2O)_n$ species formed in electrospray [141, 142]. Schwarz and coworkers have also demonstrated its formation by charge stripping from $Cu^{+}(H_2O)$ [143].

6.1. *Salt bridge mediated proton transfer vs. charge transfer*

While charge transfer is the dominant, and lowest-energy, dissociation channel for the $M^{2+}(H_2O)$ species, as soon as at least a second water molecule is present, a new, energetically more favourable proton transfer dissociation pathway becomes feasible:

$$M^{2+}(H_2O)_n \rightarrow MOH^{+}(H_2O)_{n-2} + H_3O^{+}. \tag{8}$$

This so-called charge reduction was observed as early as 1972 by Spears and Fehsenfeld [140], and this reaction usually obstructs the formation of small doubly charged hydrated metal ions by electrospray or collision-induced dissociation of larger clusters [131–133, 141]. If sufficient excess energy is present, however, the simple water loss becomes feasible to a certain extent, presumably again because of entropic effects and a much looser, more probable transition state.

While at this time we cannot study doubly ionized clusters of this type experimentally in our laboratory, we have examined the problem of the unimolecular reactivity and fragmentation of the $M^{2+}(H_2O)_2$, M = Be, Mg, Ca, Sr, Ba, dihydrate species by density functional theoretical methods [20]. It is easy to show that all of these species are metastable with respect to the above proton transfer, which is also the lowest-energy reaction pathway. In spite of this metastability, experiments have shown that the hydrated, doubly ionized clusters not only can be prepared but can survive in an ion beam or trap for a considerable length of time. The computations revealed that a considerable amount of energy has to be supplied for the charge transfer to form $M^{+}(H_2O)$ and H_2O^{+} to occur, and in the case of Ca, Sr and Ba even the simple neutral water ligand loss asymptote is lower in energy. The energetics of the dihydrates of the dications is listed in table 1. For calcium, the pathway for the salt bridge mediated charge reduction is shown in figure 9 and the corresponding potential energy surface in figure 10.

This immediately reveals the reasons for the metastability of the dihydrates: their lowest-energy dissociation follows a complex, two-step pathway. The first step requires a rather high activation barrier into an intermediate minimum to be surmounted, with one of the water ligands in the second coordination shell. In the second step, a proton transfer between the two water ligands takes place, resulting in MOH^{+} and a protonated water H_3O^{+}, followed by a Coulombic explosion and separation of the two positively charged ions.

Even though in all cases the proton transfer is the lowest-energy channel, depending on how the experiment is carried out the simple ligand loss from hydrated dications can also be observed. As discussed previously, if the 'heating' of the cluster is sufficiently slow, then it is likely that the lowest-energy pathway can be found.

Table 1. Relative energies (kJ mol^{-1}) on the $M^{2+}(H_2O)_2$ surface. Reproduced with permission from reference [20]. © 1999 American Chemical Society.

	Be	Mg	Ca	Sr	Ba
$M^+ + H_2O^+ + H_2O$	+531.3	+366.3	+489.5	+498.6	+546.3
Estimated curve crossing	+988.8	+606.3			
$M^{2+} + 2\ H_2O$	+1107.1	+639.7	+432.4	+359.8	+301.8
$M^+(H_2O) + H_2O^+$	+269.1	+236.0	+374.2	+404.1	+458.1
Estimated curve crossing	+468.0	+294.6			
$M^{2+}(H_2O) + H_2O$	+491.7	+297.1	+199.3	+167.7	+141.4
$M^{2+}(H_2O)_2$	+0.0	+0.0	+0.0	+0.0	+0.0
TS1	+275.9	+152.9	+78.0	+57.9	+40.5
Second shell		+131.9	+71.4	+56.6	+39.9
TS2		+165.0	+139.4	+157.3	+161.9
$MOH^+ + H_3O^+$	−104.8	−33.6	−65.3	−32.6	−18.6

Thus, when the energy is, as in the studies described in the preceding section, gradually supplied by many 'black-body' far-infrared photons, proton transfer should be the only reaction observed. On the other hand, when the energy is supplied by a single high-energy collision or photon, a neutral ligand loss is also likely to occur.

The reaction of dihydrated alkaline earth metal dications to form MOH^+ and H_3O^+ does not actually result in a significant change in the charge state of the metal, and there is only an indirect correlation between the metal ionization potential and its occurrence. The potential energy surface is mainly governed by simple Coulomb interactions, with the size of the cation and metal-specific changes in the distances being the important parameters. While naturally the cation size and hence also the relative energetics of the various processes depend on the specific nature of the metal, the overall character of the potentials appears to be very similar, with the arrangement with one ligand in the second solvation shell representing a local minimum for all of them except Be^{2+}. The height of the overall activation barrier for the dissociation process is determined by the second transition state which can be viewed as an M^{2+}–OH^-–H_3O^+ 'salt bridge'. In fact, its energy can be fairly well quantitatively described by this simple ionic model, with Lewis charges localized on the individual atoms. This salt bridge arrangement lowers the activation energy of the proton transfer reaction by providing a loophole on the overall potential energy surface for the escape of H_3O^+.

Similar 'salt bridge' mechanisms may be involved in a number of proton transfer processes in small solvated metal ion complexes [144–146], as well as in other ionic reactions. Especially in the electrospray process, hydrolysis reactions are operative in the formation of deprotonated ions. As one example, the generation of singly charged precursor ions for the stereoselective dissociation of metal monosaccharide complexes developed by Leary and coworkers [147–149] possibly proceeds through salt bridge transition states. In an earlier study by Solà *et al.* [150], the dominance of electrostatic interactions in the second transition state had already been identified, but the second-shell intermediate and the first transition state have not been described. Unfortunately, that work did not receive the attention it deserved and was never used to explain the aforementioned experimental studies.

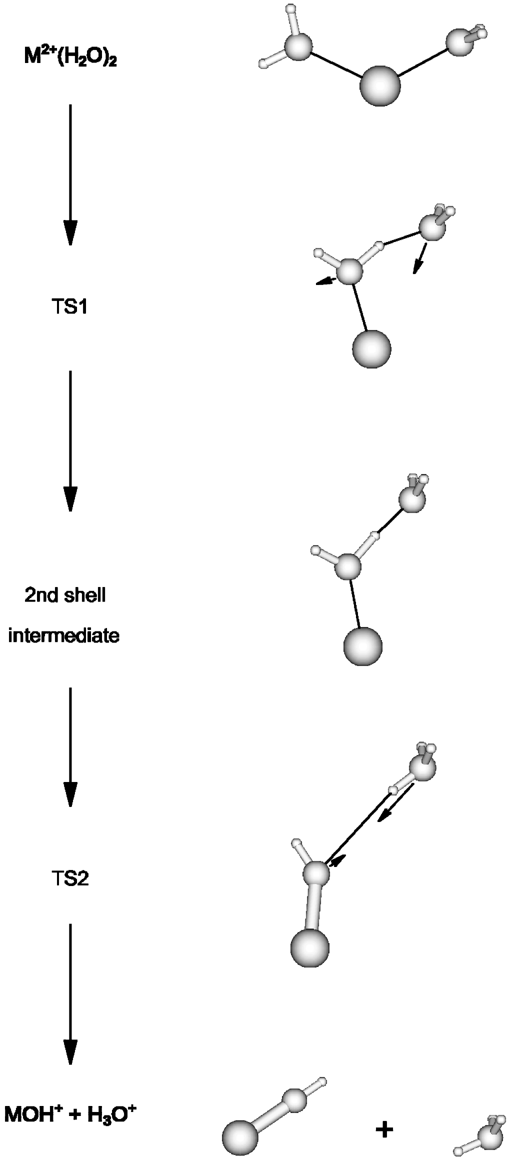

Figure 9. The general proton transfer reaction pathway for dissociation of $M^{2+}(H_2O)_2$ to produce MOH^+ and H_3O^+ for magnesium, calcium, strontium and barium. First, one water molecule is promoted from the first to the second solvation shell via transition state 1 (TS1) to form a second-shell intermediate structure. Second, proton transfer occurs via a salt bridge structure in TS2. The two charged products separate owing to Coulomb repulsion after TS2. The second-shell intermediate and TS2 do not exist for beryllium. The arrows in TS1 and TS2 indicate the reaction modes. Reproduced with permission from reference [20]. © 1999 American Chemical Society.

The validity of these conclusions for more highly hydrated systems approaching more closely bulk solution chemistry has recently been tested computationally by Vitorge and Masella [151] for $Be^{2+}(H_2O)_n$ and spectroscopically by Metz and coworkers [56, 57] for $Ni^{2+}(H_2O)_n$ and $Co^{2+}(H_2O)_n$. For both Ni and Co, the

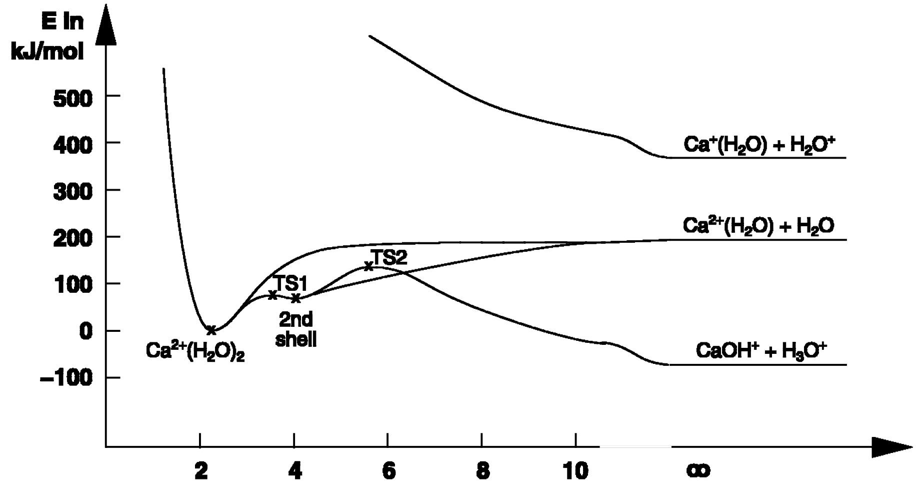

Figure 10. Potential energy surface profiles along the metal–oxygen distance as reaction coordinate for three unimolecular reaction pathways of Ca^{2+}(H$_2$O)$_2$. The curve crossings are not real; they result from the projection of a multidimensional potential energy surface on two dimensions. Reproduced with permission from reference [20]. © 1999 American Chemical Society.

proton transfer reaction was observed on photodissociation of M^{2+}(H$_2$O)$_4$ at 570 nm, yielding a single H$_3$O$^+$ and the doubly hydrated hydroxide as products:

$$M^{2+}(H_2O)_4 + h\nu \rightarrow MOH^+(H_2O)_2 + H_3O^+. \qquad (9)$$

This product formation is accompanied by a very moderate kinetic energy release of less than half the available energy. This, together with the absence of the energetically favourable H$_3$O$^+$(H$_2$O) instead of a single H$_3$O$^+$ ion, forms strong experimental support for the theoretically suggested salt bridge mechanism.

6.2. *How many water molecules can stabilize a doubly charged metal ion?*

On one hand, as already noted, many multiply charged ions are stable in bulk solutions, but it can be shown that their dihydrates, while they can be prepared and studied, are metastable. The arguments presented above indicate that there is no simple answer to this question, since, in some sense, a single water molecule stabilizes a doubly charged metal ion better than two to four water molecules, in view of the high Coulomb barrier associated with the charge transfer channel. The alternative, lower-barrier salt bridge assisted proton transfer is obviously not possible with a single ligand, but, starting with two water molecules, hydroxide formation by proton transfer and Coulomb explosion, the salt bridge mechanism [20] is energetically favourable. To what extent this is true for larger systems is so far not known, but kinetic effects and relative barrier heights seem to make it unfavourable at around four to seven water molecules for most metals. A possible exception is beryllium, for which no doubly charged hydrates in the gas phase have so far been observed.

7. Conclusions

It follows from the preceding sections that there is no simple answer to the title question; the answer would differ depending on what property of solutions one wishes to emphasize. As discussed, a proton solvated with just two or three water molecules has more in common with H^+ in solution than with a gas phase proton, a minimum of 10–12 H_2O molecules are needed to ionically dissolve a simple molecule like NaCl or HCl and, obviously, more solvent is needed for dissolving more than one solute or more complex molecules. Overall, however, the experimental studies in our laboratory and others show that clusters within the range studied of up to about 100 ligands behave in many respects already very similarly to solutions and that numerous well-known bulk reactions proceed equally well in these 'nanodroplets'. Similarly to aqueous solutions, clusters containing H^+ behave 'acidically', and those with OH^- exhibit basic properties, and the ions can participate in or catalyse chemical reactions. As in the bulk, one can clearly distinguish between soluble compounds dissociated into ions and insoluble ones, which form within the cluster an insoluble, molecular 'precipitate'.

The clusters thus provide convenient, simple and theoretically tractable systems, in which the effects of solvation and solution reactions can be studied in microscopic detail. The small 'nanodroplets' are also suitable models for studying a number of reactions important both in nature and in technology. Water-rich 'droplets' or particles participate in a number of processes in the atmosphere; their importance was demonstrated for instance both in PSC reactions and in smog formation in the troposphere. Small clusters are of course characterized by a large surface and are therefore suitable models for surface reactions. Continued studies of these systems can clearly contribute significantly to a detailed understanding of solvation effects and reactions.

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