PERSPECTIVE

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Frontiers in the infrared spectroscopy of gas phase metal ion complexes

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Received (in Montpellier, France) 26th July 2005, Accepted 29th September 2005
First published as an Advance Article on the web 25th October 2005

Studies of gas phase $M^+(L)_n$ cluster ions (where M is a metal atom and L is a ligand molecule) assist our understanding of solvation and chemical processes that involve metal ions. The recent development of pulsed, tuneable OPO (optical parametric oscillator) sources capable of generating infrared light at frequencies between 1000 and 4000 cm^{-1} has allowed the vibrational spectra of many species to be assigned for the first time. This *perspective* reviews infrared spectroscopy of metal-containing cluster ions to date and discusses future opportunities.

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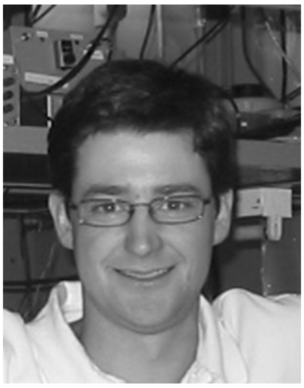

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1. Introduction

The molecular geometry and electronic structure of isolated molecules can be probed in detail through spectroscopy but the properties of isolated molecules are often difficult to connect with the properties of the related bulk material. Experiments on gas phase cluster ions allow the intervening size domain to be investigated. Clusters containing two or more metal atoms are interesting for the perspective gained on catalysis[1] and the synthesis of novel materials.[2] Studies on species containing a single metal ion inform our understanding of the structural motifs and bonding interactions found wherever a metal ion interacts with one or more neutral ligands.[3] Generation of gas phase multiply-charged metal ion complexes is a topical challenge confronted by many workers and significant advances have recently been made. These are described in recent reviews.[4,5] Both cationic[3] and anionic[6] singly-charged complexes have been studied. This *perspective* article will focus on recent advances in the experimental gas phase study of $M^+(L)_n$ species (where M is a metal atom and L is a ligand molecule) by infrared photodissociation spectroscopy. Several illustrative results will be provided. The opportunities and new challenges presented by recent developments and applications of this

DOI: 10.1039/b510678h

technique will be discussed in the context of works performed by groups throughout the world.

A principle motivation for studies on gas phase $M^+(L)_n$ complexes is the opportunity to explore the microscopic nature of solvation and the role of metal ions in biological systems. Gas phase cluster ions can be mass-selected, allowing measurements to be made as a function of the number of ligands attached to a given metal ion. Data can therefore be acquired from clusters at many different values of n. The result is a methodology sensitive to the microscopic environment at the metal ion. For example, Fuke and co-workers have shown that $Mg^+(H_2O)_n$ clusters with $n > 5$ have a significantly greater propensity to undergo proton transfer reactions than the smaller cluster ions from the series.[7] Ohshimo *et al.* identified peaks of anomalous high intensity in mass spectra of $K^+(CH_2CHCN)_n$ clusters.[8] This observation is rationalised by their proposal that an intracluster cyclisation reaction occurs within the cluster.

Spectroscopy is an especially powerful means by which details of electronic and geometric structures can be acquired as demonstrated by the work of many groups. Zero kinetic energy (ZEKE) photoelectron spectroscopy has provided details of geometric and electronic structures for some systems.[9–11] A wider range of molecules has been studied by electronic photodissociation spectroscopy.[3,7,12–18] Photodissociation is a particularly useful spectroscopic tool in the study of gas phase ions, where parent ions can be mass-selected prior to irradiation and where low number densities preclude absorption spectroscopy.

Many metal–ligand bond energies and vibrational frequencies have been established. Structural parameters have been determined from rotational constants fit to spectra.[12–18] Interpretation of spectra obtained from complexes containing alkaline earth metals can be comparatively straightforward.[12–16] Studies of those containing transition metal ions must decipher the transitions present when a wide range of different ground and excited states are possible.[17,18] Electronic spectroscopy has proven most useful in the study of complexes where a metal ion is bound to a single ligand. Although larger complexes were generated during many of the above studies, predissociation and intracluster chemical reactions frequently result in structureless spectra. Experimentalists are increasingly adopting infrared light sources to obtain spectra from cluster ions over a wider range of sizes than is possible by electronic spectroscopy.[19]

Infrared spectroscopy on cluster and molecular ions has been possible for many years using CO_2 laser sources. However, these are not well matched to the vibrational frequencies of many typical solvent molecules and photodissociation by this method usually requires the absorption of many photons. This work will review recent experiments where infrared photodissociation spectroscopy has been used to study gas phase metal ion complexes. These experiments exploit a new generation of pulsed, tuneable IR-OPO (infrared-optical parametric oscillator) sources.[20–24] The reader is referred to other reviews[19,25] for results achieved prior to 2002 and other works for results obtained using free electron laser sources.[26–28] The focus of this *perspective* will be on the most recent experiments that have exploited the tuneable range of the IR-OPO source (1000–4000 cm^{-1}) worldwide.

Tuneable IR-OPO sources with sufficient pulse energies for experiments on gas phase cluster ions have become available only recently. Infrared photodissociation spectroscopy is available to a wide range of gas phase metal ion complexes that remains comparatively unexplored to date. This is a timely opportunity to critically assess the experiments that have established the current state of research and to anticipate how future developments might further impact upon our understanding of gas phase metal ion complexes.

2. Techniques

Many of the examples presented below use a Smalley laser vaporisation source[29] coupled with supersonic expansion to generate gas phase metal ion complexes. This technique provides an opportunity to generate and select cluster ions that have low internal temperatures, enhancing the intensity and resolution of observed spectral features.[20–22,25] Hot filament sources are also used but yield complexes with higher internal energies.[23] Photodissociation experiments involve mass-selection of a given "parent" ion prior to irradiation of the selected ion using an infrared light source. Ionic fragmentation products ("daughter ions") can be identified through a subsequent stage of mass/charge analysis. Fig. 1 shows mass spectra obtained on resonance with a vibrational mode in $V^+(CO_2)_n$ complexes. In each case, the parent ion has been mass-selected prior to photofragmentation. The signal obtained with the laser "off" is subtracted from that seen with the laser "on" and the parent ion is observed as a negative-going peak owing to photodepletion. Ions that undergo photofragmentation are not transmitted to the detector with 100% efficiency. Consequently, the magnitude of the depletion in the parent ion signal does not correspond with the sum of the signal intensities of all daughter ions. The photofragmentation of $V^+(CO_2)_n$ clusters proceeds exclusively through the loss of intact CO_2 molecules.

Infrared resonance enhanced photodissociation (IR-REPD) spectra are obtained by monitoring the yield of daughter ions while scanning the laser used to photodissociate the mass-selected parent ion. IR-OPO systems are able to generate pulse energies of between 1 and 10 mJ per pulse throughout a tuneable range from 2000 to 4000 cm^{-1} within the laboratory. A linewidth of approximately 0.5 cm^{-1} is typical. Most of the

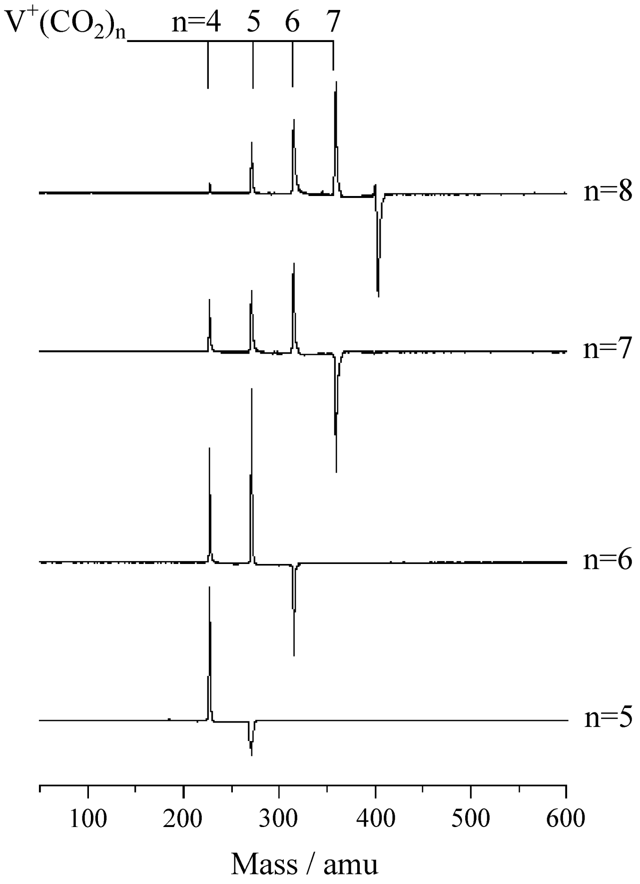

Fig. 1 Photodissociation mass spectra acquired from $V^+(CO_2)_n$ complexes. The parent ion is mass-selected prior to irradiation. The spectra are obtained by subtracting the signal yielded with the laser "off" from that obtained with the laser "on" resonance. The parent ion is observed as a negative-going peak owing to photodepletion. Photofragment ions are indicated.

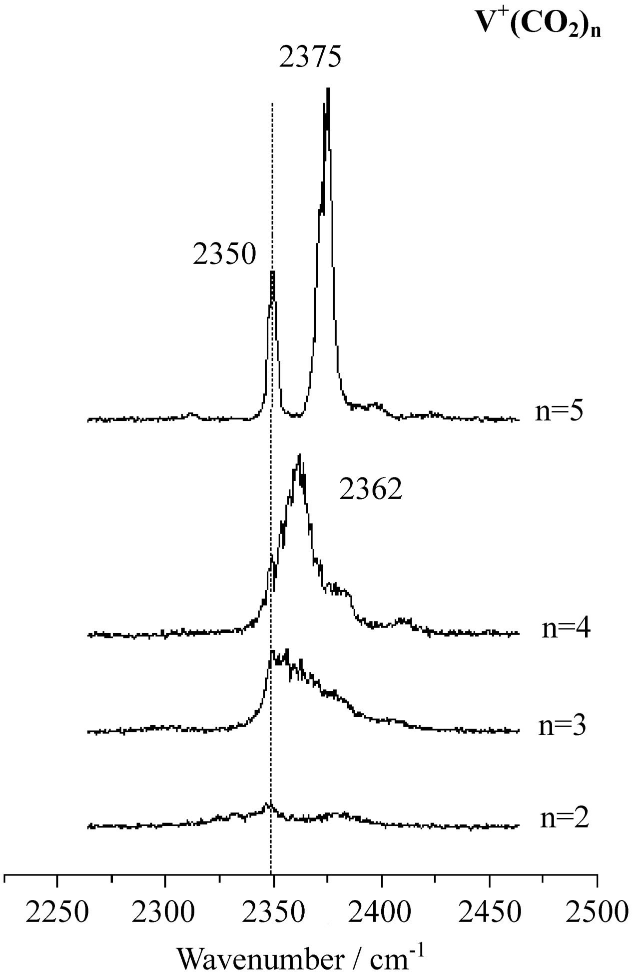

Fig. 2 The IR-REPD spectra of mass-selected $V^+(CO_2)_n$ complexes with $n = 2, 3, 4, 5$ in the fragmentation channel corresponding to the loss of a CO_2 molecule. The peak centre frequencies are indicated. The vertical dashed line indicates the frequency of the asymmetric stretch of the isolated CO_2 molecule (2349 cm^{-1}).

studies described here were not able to exploit output in the frequency interval from 1000–2000 cm^{-1}. $AgGaSe_2$ crystals are capable of generating <1 mJ per pulse within this range and have become available recently. This will extend the scope of future studies. The acquisition of infrared photodissociation spectra requires a favourable set of circumstances with respect to the bond energy of the weakest bond in the cluster (broken during photodissociation), the photon energy on resonance with the vibrational mode and the rate of intramolecular vibrational relaxation within the complex. Infrared photons are absorbed when resonant with a vibrational mode within the cluster. The deposited energy is transferred to other vibrational modes by intramolecular vibrational relaxation. If the transferred energy is sufficient to overcome the binding energy of the weakest bond, this bond breaks to yield a photofragment ion.

Infrared photodissociation spectra of small $V^+(CO_2)_n$ clusters are shown in Fig. 2.[20] Spectra are collected by monitoring the yield of the $V^+(CO_2)_{n-1}$ photofragment ion as a function of laser wavelength. The isolated CO_2 molecule has three vibrational frequencies at 1333, 667 and 2349 cm^{-1}. The symmetric stretch and degenerate bending mode of CO_2 are outside the tuneable range of the OPO source used in this experiment. However, vibrational modes are found at frequencies close to the asymmetric stretch of CO_2 at 2349 cm^{-1}. The strength of the interaction between V^+ and a single CO_2 molecule has been measured as 6050 cm^{-1} by collision-induced dissociation.[30] The weakest bond in small cluster sizes must necessarily have similar magnitude. This is greater than the energy of a single photon on resonance so multiphoton excitation must contribute to details of the observed spectra of smaller clusters. This reduces the yield and increases the width of observed features. The photofragment yield is considerably improved in the $n = 5$ and larger complexes reflecting the structures of cluster ions in the larger sizes (Fig. 3). Larger clusters must eventually contain CO_2 molecules exclusively bound to other CO_2 where bond strengths closer to that of the CO_2 dimer bond strength of ~500 cm^{-1} can be expected.[31] Thus, these infrared studies provide direct measurements on gas phase metal ion coordination numbers.

Where the strength of the weakest bond in the cluster is too high to achieve measurable photodissociation yields, the technique of "argon-tagging" can be used to obtain an infrared photodissociation spectrum. Methods where a weakly bound "messenger" species is used to allow acquisition of photodissociation spectra have been adopted by many groups since initial work by Lee and co-workers.[32–34] The symmetric and asymmetric stretches of water are found at 3657 and 3756 cm^{-1} respectively. The strength of the interaction between V^+ and a single H_2O molecule[35–37] (12280 cm^{-1}) is too high for the photodissociation of $V^+(H_2O)$ to be a single-photon process on resonance with either of the above modes. However, the bond energy of V^+–Ar is significantly lower[38] at 3100 cm^{-1}. The weakest bond in the cluster now involves the argon atom. A single photon (~3700 cm^{-1}) is enough to eject it from the

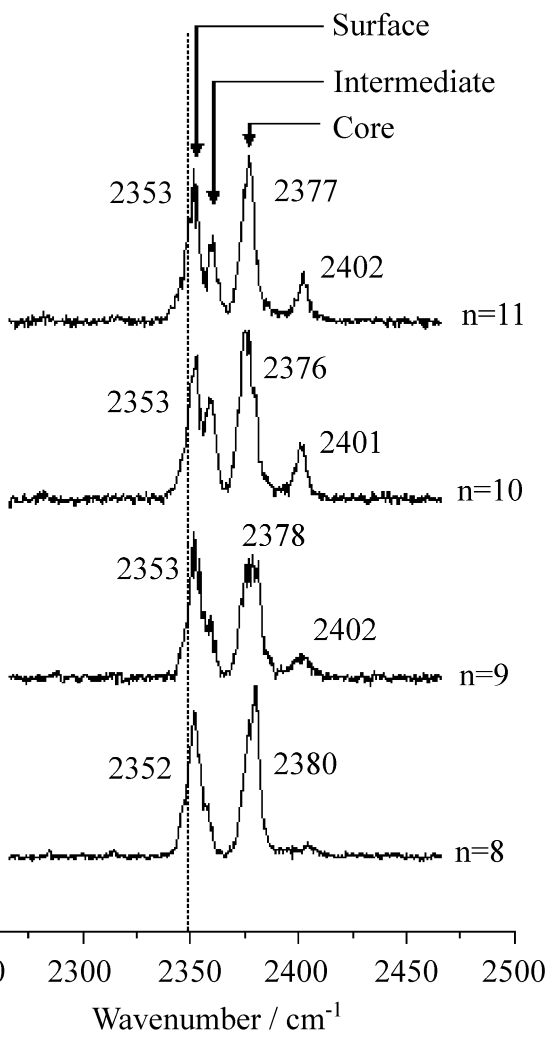

Fig. 3 The IR-REPD spectra of mass-selected $V^+(CO_2)_n$ complexes with $n = 8, 9, 10, 11$ in the fragmentation channel corresponding to the loss of a CO_2 molecule. The vertical dashed line indicates the frequency of the asymmetric stretch of the isolated CO_2 molecule (2349 cm^{-1}). The frequencies of peaks arising from CO_2 molecules in "core", "intermediate" and "surface" positions on the clusters are shown.

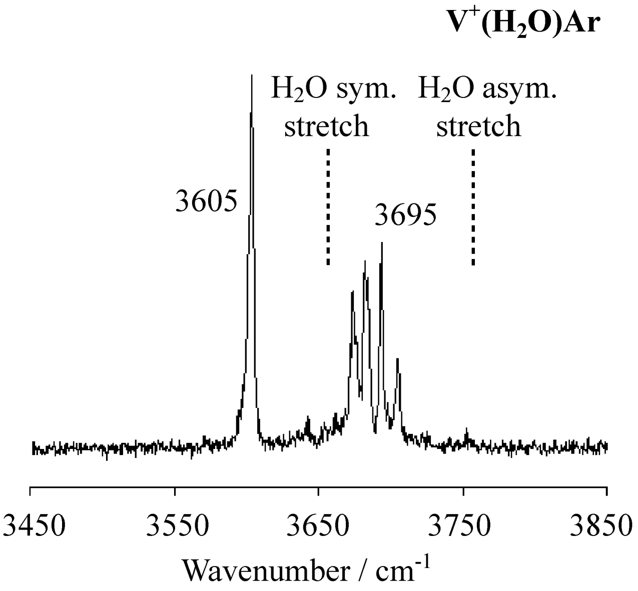

Fig. 4 The IR-REPD spectrum of $V^+(H_2O)Ar$ obtained by monitoring the yield of $V^+(H_2O)$ as a function of the wavelength of the infrared laser. The vertical dashed lines show the symmetric and asymmetric stretching modes of the isolated water molecule (3657 and 3756 cm^{-1}), respectively.

complex and a photodissociation spectrum can be acquired through monitoring the loss of argon to yield $V^+(H_2O)$. Fig. 4 shows the IR-REPD spectrum of $V^+(H_2O)Ar$. These data have been experimentally reproduced with improved S : N since an earlier publication[21] by this group.

3. $M^+(CO_2)_n$

Experiments on $Fe^+(CO_2)_n$ and $Mg^+(CO_2)_n$ are described in previous publications[39,40] and discussed in a review article.[19] These data can now be compared with the results of experiments on $Al^+(CO_2)_n$,[41] $Ni^+(CO_2)_n$,[42] $V^+(CO_2)_n$,[20] and $Si^+(CO_2)_n$.[43] The IR-REPD spectra of $V^+(CO_2)_n$ clusters are shown in Fig. 2 and 3 to allow a discussion of features typical in spectra of the wide range of $M^+(CO_2)_n$ complexes studied. During all the above experiments, information was obtained exclusively in the region of the asymmetric stretch of CO_2 at 2349 cm^{-1}. Spectra were obtained from argon-tagged $M^+(CO_2)_nAr$ complexes in addition to untagged species. The spectra of untagged complexes with $n < 5$ generally contain broad features with a low signal-to-noise (S : N) ratio while features in the spectra of argon-tagged complexes are better resolved.

Each spectrum in Fig. 2 contains a single feature that is blue-shifted by ~25 cm^{-1} with respect to the asymmetric stretch of free CO_2 (2349 cm^{-1}). This blue-shifted band provides evidence for "end-on" coordination, *via* an oxygen atom, between the metal ion and attached CO_2 molecules. The strongly repulsive wall of the metal ion's potential surface constrains the stretching motion of the CO_2 molecule, resulting in vibrational frequencies that are blue-shifted by 20–30 cm^{-1}. Both "in-phase" and "out-of-phase" combinations of the asymmetric stretching motions of individual CO_2 molecules will yield vibrational modes in $M^+(CO_2)_2$. Both of these are infrared active in a non-linear structure while only the second is infrared active where a linear geometry is adopted. A similar argument applies to the vibrational modes in $M^+(CO_2)_3$. While a trigonal planar structure will yield a single infrared active mode, further bands are observed in the spectra of non-planar structures. One band was observed in all spectra from clusters containing Fe^+, Ni^+ and V^+ with $n < 5$. This suggests that linear ($n = 1, 2$) and trigonal planar ($n = 3$) structures are adopted in $M^+(CO_2)_n$ complexes containing the above metal ions. A square-planar or tetrahedral arrangement is implied for the respective $n = 4$ complexes but the experimental data does not allow these structures to be unambiguously distinguished.

The spectra of $Mg^+(CO_2)_n$, $Al^+(CO_2)_n$ and $Si^+(CO_2)_n$ contain several bands in sizes of complex with $n < 5$. For the reasons presented above, this observation implies that non-linear and non-planar structures are present in each case. These observations can be rationalised by considering the distributions of electrons around each of these ions. The attachment of a ligand to Mg^+, Al^+ or Si^+ causes the formation of a region of high electron density immediately opposite the coordinated species.[40,41,43] This region is avoided by ligands during the addition of further molecules resulting in asymmetric clustering about the metal ion. In all cases, the magnitude of the blue-shift in modes assigned to CO_2 bound directly to the metal ion reflects the strength of the M^+–(CO_2) bond.

Two bands are observed in the spectrum of the $n = 5$ complex of $V^+(CO_2)_n$. A blue-shifted band correlates with features seen in clusters with $n < 5$. Consistent with the spectra of the smaller clusters, this is readily assigned to CO_2 bound directly to the metal ion. In addition, a new band is observed with a frequency of ~2350 cm^{-1}. It is very close in frequency to the asymmetric stretch of the free CO_2 molecule, implying that vibrations in one or more CO_2 molecules within the cluster are relatively unperturbed by interaction with the metal ion. The data therefore suggest that the fifth CO_2 molecule is the first to be attached exclusively to other CO_2 and not the metal ion, in clusters containing V^+. The fifth CO_2 molecule is significant as the first molecule to be accommodated in the second "solvation shell" of the cluster. The sharp onset of a band at ~2350 cm^{-1} was also observed in clusters containing Ni^+. The spectra of complexes of $Fe^+(CO_2)_n$, $Mg^+(CO_2)_n$, $Al^+(CO_2)_n$ and $Si^+(CO_2)_n$ also contain evidence for solvation shell formation but the onset of the band at ~2350 cm^{-1} is more gradual in these systems, appearing with steadily increasing intensity between $n = 4$ and 7.

For all complexes studied, the spectra of larger clusters ($n > 4$) have been shown to contain resonances attributable to CO_2 in several distinct environments. "Surface" modes are a result of CO_2 bound exclusively to other CO_2. "Core" modes indicate the presence of CO_2 molecules bound directly to the metal ion. "Intermediate" modes correlate with features observed during studies of pure $(CO_2)_n$ clusters[44–47] and result from CO_2 constrained by the presence of other CO_2 molecules. These features are illustrated in Fig. 3 for $V^+(CO_2)_n$ with $n = 8$–11. The signal-to-noise ratio is greater than that in the spectra of smaller complexes and the observed peaks are less broad. Unlike the "core", "intermediate" and "surface" modes, the feature at ~2402 cm^{-1} is not typical in spectra of all the metal ions studied. It is observed exclusively in the spectra of complexes containing V^+, Ni^+ and Si^+ with $n > 4$. It has consequently been suggested that intracluster chemical reactions yield MO^+ or $MO_2{}^+$ at the centre of clusters containing these ions.[20,42,43]

Metal oxide units would have high ionic character and bind to CO_2 more strongly than the corresponding metal ions. These would induce greater blue-shifts in vibrations involving CO_2 molecules at the centre of the unit. This hypothesis is most appropriate for V^+ and Si^+ where oxides are observed within the mass spectra generated by ablation of the metal target into an expanding gas mixture containing CO_2 and argon. The formation of a metal oxide at the core of a cluster containing Ni^+ has been more difficult to explain. The band (observed at 2396 cm^{-1} in complexes containing Ni^+) is present in $Ni^+(CO_2)_5$ and in larger sizes of cluster suggesting that the proportion of clusters containing metal oxide units is apparently greater in clusters larger than $Ni^+(CO_2)_5$. The implication is that the strong dipole of a metal oxide unit receives greater stabilisation through incremental solvation than does the isolated metal ion.

4. $M^+(H_2O)Ar$

The binding energy typical of an M^+–H_2O bond is greater than the energy of a photon on resonance with the stretching vibrational modes of water at 3657 and 3756 cm^{-1}. It is therefore necessary to use argon-tagging to study $M^+(H_2O)$ complexes as described in Section 2. In all cases, studies have been performed in the region of the symmetric (3657 cm^{-1}) and asymmetric (3756 cm^{-1}) stretches of the water molecule. Lisy and co-workers used a resistively heated filament covered in a paste containing alkali metal salts to generate $M^+(H_2O)Ar$ complexes where M = Na, K, Cs.[48]

The metal ion–dipole interaction withdraws binding electron density from the water, weakening the O–H bonds and reducing the frequencies of its vibrational modes. Hence, bands corresponding to both the symmetric and asymmetric stretches of water are red-shifted by ~20 cm^{-1} (symmetric stretch) and ~45 cm^{-1} (asymmetric stretch) with respect to their positions in free H_2O. The measured red-shift is marginally greater in the smaller ions, reflecting their greater electronegativity and hence stronger cation–water interaction. The A rotational constants of the molecules studied correspond directly with the B rotational constant of the isolated water molecule. In each case, the A rotational constant was determined through simulation and fitting of the rotational contour. The results provide information on the molecular structure adopted by the complex. Attachment of water to the metal ion was observed to decrease the rotational constant about the principal axis by <0.5 cm^{-1}. Although it is possible that the H–O–H bond angle of water changes slightly on attachment to M^+, the authors suggest that the measured change is too great to result from a change in the geometry of water. They conclude that the position of the argon atom, which is off-axis in the vibrationally-averaged structure of the complex, leads to the low value for the rotational constant determined.

The internal energies of the species were determined from simulation of the various band contours as a function of temperature. It was found that the ions cool most effectively where the binding energy between the ion and water molecule is smallest. The resistive filament source used to generate $M^+(H_2O)Ar$ during the above experiments necessarily generates clusters with comparatively high internal temperatures. Laser vaporisation sources offer an alternative means of generating $M^+(H_2O)Ar$ units that have cooler internal temperatures, thus yielding more highly resolved and intense spectra.

The infrared photodissociation spectrum of $V^+(H_2O)Ar$ is shown in Fig. 4. Transitions in the symmetric stretching mode of free water are "parallel" (a-type) transitions in which the transition dipole moment is parallel to the axis of symmetry. Those associated with the asymmetric stretch are "perpendicular" (b-type) transitions in which the transition dipole moment and axis of symmetry are mutually perpendicular. Different selection rules are associated with each type of transition. The band structure in the symmetric stretch of $V^+(H_2O)Ar$ at ~3605 cm^{-1} is assigned readily by assuming the selection rules that apply to parallel bands. It was suggested that coordination of water to the metal results in an increased H–O–H bond angle (from 110 to 113.8 degrees). The structure observed in the band corresponding to the asymmetric stretch of $V^+(H_2O)Ar$, between 3670 and 3710 cm^{-1} cannot be so readily explained. Where parameters determined from simulation of the symmetric stretch are assumed, the rotational constant of the excited state is too small to be purely the result of an expanded H–O–H angle. In addition, the band is a "hybrid" band that contains contributions from selection rules for both "parallel" and "perpendicular" bands. These observations were rationalised by considering the energetics of V^+ insertion into an O–H bond.[35–37]

A hybrid band can be expected where the geometry of a given complex changes as a direct result of excitation in a specific vibrational mode, so as to change the relative ordering of the moments of inertia of a given molecule.[49] If a small change in the geometry of the molecule on excitation were sufficient to realign its dipole moment, this would cause the argon atom to move to an "off-axis" position and yield a significantly reduced rotational constant. The energy of the product resulting from insertion of V^+ into an O–H bond in water is ~5 kcal mol^{-1} higher than that of the V^+–H_2O species.[35–37] This increment is lower than the energy of a single photon on resonance with the asymmetric stretch of water. Several reports describe chemical reactions driven by excitation in a specific vibrational mode.[49–51] It was therefore suggested that excitation in the asymmetric stretching mode of $V^+(H_2O)Ar$ might initiate an insertion process to yield a transition state[52] with a rotational constant of comparable magnitude to that determined for $V^+(H_2O)Ar$ in the (v = 1) excited state.

5. Isomeric structures in $M^+(H_2O)_nAr_m$

Many experiments have demonstrated that the resolution and S : N ratio of peaks identified from argon-tagged complexes, such as $V^+(H_2O)Ar$, are greater than from comparable untagged species.[20,41–43] In general, the positions of absorption bands measured for argon-tagged species are shifted only 5–10 cm^{-1} with respect to those of untagged species. However, where the M^+–Ar binding energy is significant compared with the M^+–L binding interaction, it cannot necessarily be assumed that the spectrum of an argon-tagged complex is representative of the untagged species. The spectrum acquired from $V^+(H_2O)Ar$ confirms that argon is initially attached directly opposite the oxygen atom in the water molecule in this species. However, this assumption is not appropriate to all metal ion complexes open to study.[22] Investigations of the attachment of argon to metal ion complexes are clearly necessary in order to underpin future investigations that will employ argon-tagging. Experiments to investigate the different isomeric structures of $M^+(H_2O)Ar_m$ complexes have been made by several groups.[22,53,54]

Inefficient photodissociation was observed from $Fe^+(H_2O)Ar$ and an IR-REPD spectrum could not be obtained from this species.[53] An IR-REPD spectrum of $Fe^+(H_2O)Ar_2$ was obtained, but bands in this spectrum show no rotational contour. This is a consequence of a low rotational constant caused by the location of the second argon atom in an "off-axis" position with respect to the C_2 axis of $Fe^+(H_2O)$. The infrared spectrum of this species was shown to contain more distinct bands than expected in the OH region. Each band is red-shifted with respect to the OH stretching vibrations of the isolated water molecule. It is necessary to assume that several isomeric structures contribute to these features. Firstly, one or both argon atoms may attach to the metal ion. It is suggested that the spectrum of $Fe^+(H_2O)Ar_2$ also contains contributions from isomers where one or both argon atoms are attached to hydrogen atoms on the water molecule. Experiments on $Fe^+(H_2O)_2Ar$ suggest that isomeric structures (with respect to the position of the water atom) also contribute to the observed spectra of this species.[53]

Several groups have obtained infrared spectra for $Mg^+(H_2O)_n$ clusters containing one or more argon atoms. Inokuchi and co-workers performed experimental and theoretical studies on $Mg^+(H_2O)_{1–4}$, $Mg^+(H_2O)_{1–4}Ar$ and $Al^+(H_2O)_{1,2}Ar$.[54] These clusters were generated with comparatively high internal energies, as demonstrated by broadening in the acquired spectra and the measurable yield achieved from photodissociation of $Mg^+(H_2O)$. The bond energy of this complex is known to be significantly higher than the energy of a single photon on resonance, suggesting that clusters already have high internal energies prior to absorption and photofragmentation. The spectra acquired from argon-tagged

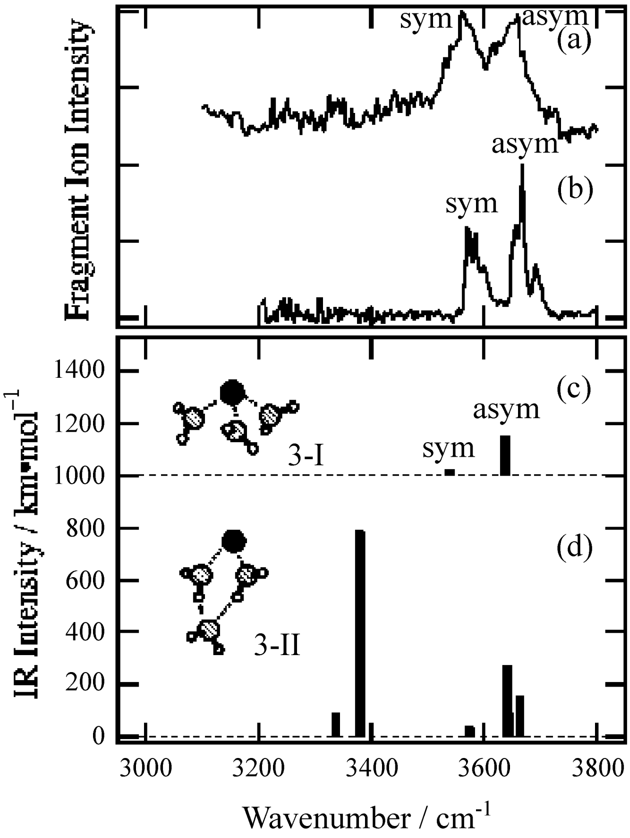

Fig. 5 Reprinted with permission from Inokuchi *et al.*[54b] Copyright (2004) American Chemical Society. (a) The IR-REPD spectra of $Mg^+(H_2O)_3$ with the positions of the symmetric (3657 cm^{-1}) and asymmetric (3756 cm^{-1}) stretches of the water molecule indicated. (b) The IR-REPD spectra of $Mg^+(H_2O)_3Ar$. (c) Spectrum calculated using DFT at the B3LYP/6-31+G* level for $Mg^+(H_2O)_3$ with three H_2O attached directly to the metal ion. (d) Spectrum calculated (as above) with two H_2O attached to the metal ion and one molecule located in a bridging site in the second solvation shell.

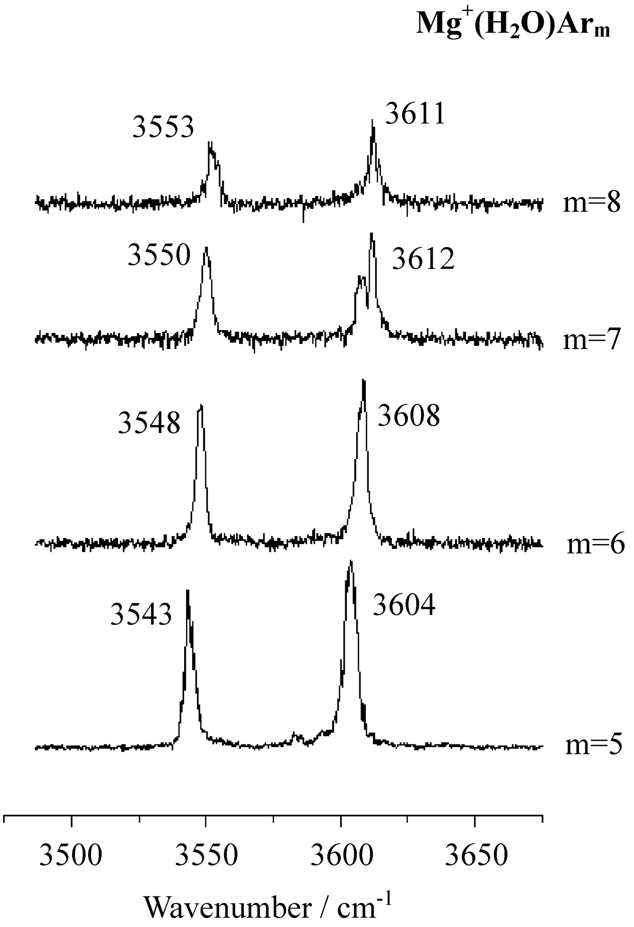

Fig. 6 The IR-REPD spectra of $Mg^+(H_2O)Ar_m$ with $m = 5, 6, 7, 8$, with peak centre frequencies indicated.

species are better resolved, demonstrating that cooler temperatures can be expected in argon-tagged clusters. All bands are red-shifted with respect to the vibrational frequency of the isolated water molecule. The data in Fig. 5 were presented by Inokuchi *et al.* within the recent report on the infrared spectroscopy of $Mg^+(H_2O)_{1-4}$ complexes.[54b] Infrared photodissociation spectra of $Mg^+(H_2O)_3$ and $Mg^+(H_2O)_3Ar$ obtained experimentally are compared with spectra calculated for two different isomeric forms of the three-coordinate complex. The reduced broadening and improved S : N ratio typical of data acquired from argon-tagged species is evident in the figure. The isomeric structures for which spectra were calculated are distinguished by the number of water molecules in the first solvation shell. The calculated spectrum where three water molecules are directly attached to the metal ion is most consistent with the experimental data. The study identified evidence of water–water bonds in clusters with $n > 3$ and concluded that the solvation number of the hydrated magnesium ion is three. The study on $Al^+(H_2O)_{1,2}Ar$ and $Mg^+(H_2O)_{1,2}Ar$ clusters found that H_2O molecules are bound exclusively to the metal ion in all species examined. The authors conclude that an intracluster reaction occurs to yield an $HOAl^+H$ unit within $Al^+(H_2O)_2Ar$.

The spectra of $Mg^+(H_2O)Ar_m$ complexes were studied by Duncan and co-workers for $m = 1$–9. Some of these data were published in a previous work[22] and are reproduced herein. All of the observed bands are red-shifted with respect to the stretching vibrations of the free water molecule. The magnitude of the red-shift is dependent upon the particular value of m. Previous experiments and theory[55] have shown that attachment of H_2O to Mg^+ causes the formation of a region of high electron density immediately opposite H_2O.[56] As a consequence, argon atoms in $Mg^+(H_2O)Ar_m$ do not attach directly opposite the water molecule. In smaller clusters ($m < 4$), data show evidence for several isomers distinguished by the position of the argon atom. In larger clusters, argon atoms eventually surround the cluster and the spectral shifts converge to a value that is approximately constant with respect to the number of argon atoms (Fig. 6). The observation of several structural isomers of $Mg^+(H_2O)Ar_m$ confirms that infrared photodissociation spectra acquired from argon-tagged metal ion complexes may not always be representative of the character of the analogous untagged complexes.

6. $Mg^+(NH_3)_n$ and $Mg^+(CH_3OH)_n$

The infrared photodissociation spectroscopy of $Mg^+(NH_3)_n$ has been reported by Ohashi *et al.*[57] The results of experiments were compared with theoretical calculations in order to provide details of the structures of clusters with $n = 3$–6. The calculations show that a single hydrogen bond between NH_3 molecules would yield a band that is significantly red-shifted (by ~400 cm^{-1}) with respect to the N–H stretching frequency at ~3337 cm^{-1}. The photodissociation experiments found bands only from 3250–3400 cm^{-1}, suggesting that all NH_3 molecules are bound to the metal ion in $Mg^+(NH_3)_3$. Studies of the $n = 4$ and 5 complexes suggest that all NH_3 molecules are also bound to the metal ion in these larger species but red-shifted bands present in low intensity also provide evidence for NH_3 in bridging sites in a second solvation shell. These bridging molecules bind to several NH_3 in the first solvation shell through multiple hydrogen bonds. The evidence that as many as five molecules coordinate with Mg^+ before subsequent molecules are added to the second shell is in contrast with the data acquired from $Mg^+(H_2O)_n$ clusters.

A study of $Mg^+(CH_3OH)_n$ where $n = 1$–4 found that three molecules comprise the first solvation shell.[58] The fourth molecule occupies a position in the second solvation shell and forms hydrogen bonds to CH_3OH attached directly to the metal ion. This conclusion is consistent with the data acquired from $Mg^+(H_2O)_n$. As described above, a coordination number of three was identified for H_2O attached to the Mg^+ ion.

7. $M^+(C_2H_2)_n$

The results of experiments on $Ni^+(C_2H_2)_n$ clusters were discussed in a previous paper[59] and review article.[19] While the symmetric stretch of the free C_2H_2 molecule is not infrared active, the presence of the metal ion induces a change in the geometry of the C_2H_2 unit causing it to become infrared active. It was suggested that bands in the spectrum of larger $Ni^+(C_2H_2)_n$ contain evidence for an intracluster cyclisation reaction.

Recent work has extended the range of metal ions examined to include V^+, Fe^+ and Co^+.[60] Vibrational spectra were obtained in the region of the C_2H_2 symmetric and asymmetric stretches for $V^+(C_2H_2)Ar$, $Fe^+(C_2H_2)Ar$ and $Co^+(C_2H_2)Ar$. Red-shifted bands are identified in all the spectra collected, consistent with bonding through the Dewar–Chatt–Duncanson π-bonding mechanism. Ligands donate electron density to the empty metal orbitals and receive electron density into π* orbitals through back-donation from the metal. This weakens the bonding within the acetylene unit and causes red-shifts in vibrational modes. Theory[60] predicts that metal ions in complexes containing the late transition metals (Fe^+, Ni^+, Co^+) adopt high multiplicity states and bind to C_2H_2 mainly through electrostatic interactions. Only a small contribution is expected from the Dewar–Chatt–Duncanson mechanism.

The red-shifts associated with the vibrational modes of $V^+(C_2H_2)_n$ clusters are greater than those identified in spectra of the other $M^+(C_2H_2)_n$ species. Theory predicts some covalent interaction and more significant π–π* back-bonding when C_2H_2 binds to early transition metals, accounting for the greater red-shifts of the observed modes in $V^+(C_2H_2)$. Shorter M^+–C bonds, longer C–C distances and metal ions in states of lower multiplicity are predicted. Both theory and experiment are consistent with the hypothesis that $V^+(C_2H_2)$ contains a three-membered ring metallacycle with C–H stretching frequencies similar to cyclopropene.

8. $M^+(C_6H_6)_n$

Infrared spectra were acquired for a variety of $M^+(C_6H_6)_n$ complexes by using a free electron laser source to probe ring distortion and C–H bending modes.[61] Since publication of this work, $Ni^+(C_6H_6)_n$, $V^+(C_6H_6)_n$ and $Si^+(C_6H_6)_n$ clusters have been studied using an IR-OPO to excite C–H stretching vibrational modes. The ν_{12} fundamental is accidentally degenerate with $\nu_{13} + \nu_{16}$ and $\nu_2 + \nu_{13} + \nu_{16}$ combination bands in liquid benzene, yielding the Fermi triad of peaks at $\sim 3070\ cm^{-1}$ in the infrared spectrum of the liquid substance. The triad is also present in the spectrum of the gaseous molecule. In each of the studies described below, the attachment of a metal ion to a single benzene molecule was found to change the vibrational frequencies of C_6H_6 enough to break the degeneracy that yields the Fermi triad in the liquid substance. Hence, only single bands are observed in spectra of the smallest complexes while multiple peaks (arising from Fermi resonances) are observed in those larger complexes where benzene molecules are present but not attached to the metal ion.

Photodissociation spectra were obtained for $Si^+(C_6H_6)_n$ cluster ions[62] with $n > 1$. Spectra of argon-tagged $Si^+(C_6H_6)_nAr$ complexes were also obtained and were found to provide superior signal-to-noise ratios. All bands are slightly blue-shifted with respect to the position of C–H stretching modes in the isolated C_6H_6 molecule. This is surprising given the Dewar–Chatt–Duncanson model of bonding expected in metal ion complexes containing C_6H_6 and observed in complexes of $M^+(C_2H_2)_n$. The photofragmentation yields attained in spectra of $Si^+(C_6H_6)_{1,2}$ confirm that the first benzene molecule attaches to the metal ion more strongly than the second and that subsequent addition of benzene yields comparatively weak bonds. A single band is observed in the spectrum of each complex with $n < 3$. A multiplet is present in the spectra of larger complexes, indicating that no more than two molecules can attach directly to the metal ion in a "sandwich" structure. Additional ligands bind to other C_6H_6 molecules.

Studies of $V^+(C_6H_6)_{1,2}$ required argon tagging to identify resonances in the C–H stretching region close to $3100\ cm^{-1}$.[63] Larger complexes dissociate readily. Resonances corresponding to C–H stretch vibrations are identified in positions that are blue-shifted with respect to those in the isolated C_6H_6 molecule. A single band is observed in the spectra of $V^+(C_6H_6)_{1,2}Ar$ molecules while a multiplet of three is seen in larger complexes, suggesting that a maximum of two benzene molecules attach directly to the metal ion in a "sandwich" structure.

Studies of $Ni^+(C_6H_6)_n$ found that argon-tagging was necessary to obtain measurable photodissociation yields from the $n = 1,2$ complexes.[64] Spectra of small, argon-tagged clusters contain a band that is blue-shifted with respect to the C–H stretching frequency of free C_6H_6, as seen with the assigned vibrational modes of $V^+(C_6H_6)_{1,2}Ar$ and $Si^+(C_6H_6)_{1,2}Ar$. Both observations are consistent with polarisation of electron density from benzene towards the metal ion. Larger clusters contain a larger number of bands and photodissociate more readily, showing that Ni^+ adopts the two-coordinate "sandwich" structures also identified for V^+ and Si^+. In the case of Ni^+, the benzene ring undergoes distortion on coordination.

9. $M^+(N_2)_n$

The vibrational mode of a free N_2 molecule is not infrared active because the dipole moment of the molecule is unchanging throughout the period of vibration. Attachment to a metal ion causes the mode to become infrared active as a consequence of the induced dipole, as demonstrated by a recent study[65] on $V^+(N_2)_n$. This study provided the first infrared spectrum acquired from a gas phase complex containing a metal ion bound to N_2. Further studies involving Fe^+ and other metals could potentially shed light on the process of nitrogen fixation.

A single peak was identified in the spectra of small $V^+(N_2)_n$ complexes in a position that is red-shifted by $\sim 70\ cm^{-1}$ with respect to that of the N_2 vibrational frequency. In conjunction with density functional theory, this result was found to provide strong evidence for N_2 coordinated *via* an "end-on" interaction to a metal ion that occupies a quintet state. On resonance, the loss of N_2 molecules from clusters with $n > 6$ was found to terminate in the formation of $V^+(N_2)_6$, suggesting a coordination number of six for the V^+ ion. Calculations suggest the structure of the four-coordinate complex is square planar and that $n = 5$ and $n = 6$ complexes have slightly distorted square pyramidal and octahedral geometries.

10. Competitive solvation of $M^+(X)_n(Y)_m$

Infrared spectroscopy provides an opportunity to study structural effects and chemical reactions in complexes where several solvent molecules are attached to the same metal ion. Lisy and co-workers have used IR-OPO sources to study competitive solvation in $Na^+[(CH_3)_2CO]_n(CH_3OH)_m$, $M^+(H_2O)_n(C_6H_6)_m$,

$Na^+(H_2O)_n(C_6F_6)_m$ and $M^+(H_2O)_n(CH_3CN)_m$, where M is Na^+ or K^+.[66–69]

The study of $Na^+[(CH_3)_2CO]_n(CH_3OH)_m$ used a combination of unimolecular loss measurements and infrared spectroscopy to provide information about the structures of the clusters.[66] It was found that the first solvation shell consists of six molecules, but that CH_3OH forms hydrogen bonds with other molecules before completion of the first solvation shell. Loss from clusters with $m = 1$, $n > 6$ exclusively involves the detachment of $(CH_3)_2CO$, indicating that methanol occupies a position within the first solvation shell at all sizes of cluster. The competition for coordination sites between C_6H_6 and H_2O attached to Na^+ or K^+ was also examined in several papers.[67] It was found that the interaction between C_6H_6 and the metal ion is strong enough to displace several H_2O molecules from the hydration shell of K^+. In contrast, water molecules in the hydration shell around Na^+ are not replaced by competing benzene molecules. These experiments are particularly significant in view of the transfer of hydrated Na^+ and K^+ through ion channels.

Experiments on $Na^+(H_2O)_n(C_6F_6)_m$ clusters found no evidence for vibrational modes corresponding to H-bonded water in small cluster sizes.[68] Bands corresponding to the symmetric and asymmetric stretching modes of H_2O are red-shifted from their positions in free H_2O reflecting its interaction with the Na^+ cation. In clusters containing one or four water molecules, the addition of up to nine C_6F_6 ligands did not yield evidence of interaction between C_6F_6 and H_2O molecules. These observations suggest a separation of phases on the microscopic scale, with H_2O and C_6F_6 participating in different bonding networks. The study of $M^+(H_2O)_n(CH_3CN)_m$ complexes ($M = Na^+, K^+$) showed that coordination of CH_3CN to the metal ion affects the strengths of interactions between the metal ion and water molecules and also between the water molecules themselves.[69] Theory was used to calculate the infrared spectra expected from clusters of different structures and was compared with the experimental spectra to identify trends.

11. Perspectives

Infrared photodissociation spectroscopy provides a powerful technique capable of providing information on a wide range of phenomena. Studies of $M^+(CO_2)_n$ complexes have yielded evidence that intracluster chemical reactions to form metal oxides within clusters are size-dependent. Experiments on $M^+(H_2O)Ar$ have shown how bond lengths and angles in the water molecule change as a consequence of coordination to a metal ion and have suggested that vibrational excitation in the asymmetric stretching mode of $V^+(H_2O)Ar$ initiates chemical reaction. It has been shown that several isomeric forms of $Fe^+(H_2O)Ar_{1,2}$ and $Mg^+(H_2O)Ar_{1-9}$ complexes can be generated. Infrared spectra of $M^+(C_2H_2)_n$ and $M^+(C_6H_6)_n$ reflect the Dewar–Chatt–Duncanson mechanism that binds these complexes and have provided details of the clusters' structures. Studies of complexes containing C_2H_2 have revealed possible evidence of intracluster cyclisation reactions. A study of $V^+(N_2)_n$ has confirmed that N_2 binds to the metal ion in an end-on configuration and that six molecules comprise the first solvation shell. Studies of $M^+(X)_n(Y)_m$ complexes have identified examples of microscopic phase separation.

The scope of this technique is continually being extended to new ligands and metal ions. Of the ligands listed above, water is most fundamental in conventional solution phase chemistry. It can be anticipated that many studies will be devoted to elucidating the structure of gas phase water-containing $M^+(L)_n$ complexes during the next few years. Complexes containing H_2, C_2H_4, CH_3OH and other alcohols, and CH_3CN and other nitriles are also likely to be studied in conjunction with transition metal ions. Studies of $M^+(X)_n(Y)_m$ complexes that contain transition metal ions can also be expected.

Research will continue to benefit from improvements in technology appropriate to the experiments. The manufacture of optically active $AgGaSe_2$ crystals capable of generating pulsed, tuneable, infrared light at frequencies below 2000 cm^{-1} has already made additional vibrational modes accessible and expanded the scope of research. This development provides researchers with access to the IR fingerprint region using a benchtop laser system. Gerhards and co-workers have described the application of an $AgGaSe_2$ crystal to generate 1000–1800 cm^{-1} output from an OPO for the study of C=O vibrations in peptides.[70] Headrick *et al.*[71] recently reported studies of $H^+(H_2O)_n$ clusters from n = 1–11. Vibrational modes within the clusters were excited using the output of an OPO between 1000 and 4000 cm^{-1}. This technology will surely be applied to study clusters containing metal ions within the near future. The rapid advances made during the last ten years are likely to be followed and superseded by exciting new developments during the remainder of the decade. Indeed, an accelerating rate of progress can be expected.

Acknowledgements

The authors gratefully acknowledge support from the US Department of Energy (Grant No. DE-FG02–96ER14658) and National Science Foundation (Grant No. CHE-0244143). NRW thanks the Royal Society (UK) for the award of a University Research Fellowship.

References

1 S. Lee, C. Y. Fan, T. P. Wu and S. L. Anderson, *J. Phys. Chem. B*, 2005, **109**, 381.
2 S. Nagao, A. Kato, A. Nakajima and K. Kaya, *J. Am. Chem. Soc.*, 2000, **122**, 4221.
3 M. A. Duncan, *Annu. Rev. Phys. Chem.*, 1997, **48**, 69.
4 R. B. Metz, *Int. J. Mass. Spectrom.*, 2004, **235**, 131.
5 A. J. Stace, *J. Phys. Chem. A*, 2002, **106**, 7993.
6 K. Hashimoto, T. Kamimoto and K. Fuke, *Chem. Phys. Lett.*, 1997, **266**, 7.
7 (*a*) F. Misaizu, M. Sanekata, K. Tsukamoto, K. Fuke and S. Iwata, *J. Phys. Chem.*, 1992, **96**, 8259; (*b*) F. Misaizu, M. Sanekata, K. Tsukamoto and S. Iwata, *Z. Phys. D: At., Mol. Clusters*, 1993, **26**, S180; (*c*) F. Misaizu, M. Sanekata, K. Fuke and S. Iwata, *J. Chem. Phys.*, 1994, **100**, 1161; (*d*) M. Sanekata, F. Misaizu, K. Fuke, S. Iwata and K. Hashimoto, *J. Am. Chem. Soc.*, 1995, **117**, 747.
8 K. Ohshimo, F. Misaizu and K. Ohno, *J. Chem. Phys.*, 2002, **117**, 5209.
9 (*a*) D. A. Rodham and G. A. Blake, *Chem. Phys. Lett.*, 1997, **267**, 522; (*b*) K. H. Wang, D. A. Rodham, V. McKoy and G. A. Blake, *J. Chem. Phys.*, 1998, **108**, 4817.
10 (*a*) S. G. Li, J. F. Fuller, B. R. Sohnlein and D. S. Yang, *J. Chem. Phys.*, 2003, **119**, 8882; (*b*) S. G. Li, B. R. Sohnlein, G. K. Rothschopf, J. F. Fuller and D. S. Yang, *J. Chem. Phys.*, 2003, **119**, 5406; (*c*) J. Miyawaki, D. S. Yang and K. Sugawara, *Chem. Phys. Lett.*, 2003, **372**, 627.
11 J. K. Agreiter, A. M. Knight and M. A. Duncan, *Chem. Phys. Lett.*, 1999, **313**, 162.
12 (*a*) M. R. France, S. H. Pullins and M. A. Duncan, *J. Chem. Phys.*, 1998, **109**, 8842; (*b*) J. E. Reddic and M. A. Duncan, *J. Chem. Phys.*, 1999, **110**, 9948; (*c*) J. E. Reddic and M. A. Duncan, *J. Chem. Phys.*, 2000, **112**, 4974; (*d*) M. A. Duncan, *Int. J. Mass Spectrom.*, 2000, **200**, 545.
13 (*a*) G. S. Fanourgakis, S. C. Farantos, C. Luder, M. Velegrakis and S. S. Xantheas, *J. Chem. Phys.*, 1998, **109**, 108; (*b*) D. Prekas, B. H. Feng and M. Velegrakis, *J. Chem. Phys.*, 1998, **108**, 2712; (*c*) C. Luder and M. Velegrakis, *J. Chem. Phys.*, 1996, **105**, 2167.
14 (*a*) W. Y. Lu, T. H. Wong, Y. Sheng and P. D. Kleiber, *J. Chem. Phys.*, 2003, **118**, 6905; (*b*) W. Y. Lu, T. H. Wong, Y. Sheng, A. T. Lytle and P. D. Kleiber, *J. Phys. Chem. A*, 2003, **107**, 984; (*c*) Y. Lu, T. H. Wong, Y. Sheng and P. D. Kleiber, *J. Chem. Phys.*, 2002, **117**, 6970.
15 (*a*) J. I. Lee, D. C. Sperry and J. M. Farrar, *J. Chem. Phys.*, 2004, **121**, 8375; (*b*) J. I. Lee and J. M. Farrar, *J. Phys. Chem. A*, 2002, **106**, 11886; (*c*) J. I. Lee, D. C. Sperry and J. M. Farrar, *J. Chem. Phys.*, 2001, **114**, 6180.

16 (*a*) W. Guo, H. Liu and S. Yang, *Int. J. Mass Spectrom.*, 2003, **226**, 291; (*b*) H. Liu, S. Yang, X. Zhang and Y. Wu, *J. Am. Chem. Soc.*, 2003, **125**, 12351; (*c*) W. Guo, H. Liu and S. Yang, *J. Chem. Phys.*, 2002, **117**, 6061.

17 (*a*) R. L. Asher, D. Bellert, T. Buthelezi and P. J. Brucat, *Chem. Phys. Lett.*, 1994, **224**, 529; (*b*) R. L. Asher, D. Bellert, T. Buthelezi, G. Weerasekera and P. J. Brucat, *Chem. Phys. Lett.*, 1994, **228**, 390; (*c*) D. Bellert, T. Buthelezi, K. Dezfulian, T. Hayes and P. J. Brucat, *Chem. Phys. Lett.*, 1996, **260**, 458.

18 (*a*) K. L. Stringer, M. Citir and R. B. Metz, *J. Phys. Chem. A*, 2004, **108**, 6996; (*b*) R. B. Metz, *Int. Rev. Phys. Chem.*, 2004, **23**, 79; (*c*) C. J. Thompson, K. L. Stringer, M. McWilliams and R. B. Metz, *Chem. Phys. Lett.*, 2003, **376**, 588.

19 M. A. Duncan, *Int. Rev. Phys. Chem.*, 2003, **22**, 407.

20 N. R. Walker, R. S. Walters and M. A. Duncan, *J. Chem. Phys.*, 2004, **120**, 10037.

21 N. R. Walker, R. S. Walters, E. D. Pillai and M. A. Duncan, *J. Chem. Phys.*, 2003, **119**, 10471.

22 N. R. Walker, R. S. Walters, C.-S. Tsai, K. D. Jordan and M. A. Duncan, *J. Phys. Chem. A*, 2005, **109**, 7057.

23 (*a*) T. D. Vaden and J. M. Lisy, *J. Chem. Phys.*, 2004, **120**, 721; (*b*) C. J. Weinheimer and J. M. Lisy, *J. Phys. Chem.*, 1996, **100**, 15305.

24 Y. Inokuchi, K. Ohshimo, F. Misaizu and N. Nishi, *J. Phys. Chem. A*, 2004, **108**, 5034.

25 J. M. Lisy, *Int. Rev. Phys. Chem.*, 1997, **16**, 267.

26 T. D. Fridgen, T. B. McMahon, L. MacAleese, J. LeMaire and P. Maitre, *J. Phys. Chem. A*, 2004, **108**, 9008.

27 G. v. Helden, D. v. Heijnsbergen and G. Meijer, *J. Phys. Chem. A*, 2003, **107**, 1671.

28 D. T. Moore, J. Oomens, J. R. Eyler, G. v. Helden, G. Meijer and R. C. Dunbar, *J. Am. Chem. Soc.*, 2005, **127**, 7243.

29 T. G. Dietz, M. A. Duncan, D. E. Powers and R. E. Smalley, *J. Chem. Phys.*, 1981, **74**, 6511.

30 M. R. Sievers and P. B. Armentrout, *J. Chem. Phys.*, 1995, **102**, 754.

31 R. Bukowski, J. Sadlez, B. Jeziorski, P. Jankowski, K. Szalewicz, S. A. Kucharski, H. L. Williams and B. M. Rice, *J. Chem. Phys.*, 1999, **110**, 3785.

32 (*a*) M. Okumura, L. I. Yeh and Y. T. Lee, *J. Chem. Phys.*, 1985, **83**, 3705; (*b*) M. Okumura, L. I. Yeh and Y. T. Lee, *J. Chem. Phys.*, 1988, **79**, 88.

33 (*a*) M. Meuwly, S. A. Nizkorodov, J. P. Maier and E. J. Bieske, *J. Chem. Phys.*, 1996, **104**, 3876; (*b*) O. Dopfer, D. Roth and J. P. Maier, *J. Phys. Chem. A*, 2000, **104**, 11702; (*c*) E. J. Bieske and O. Dopfer, *Chem. Rev.*, 2000, **100**, 3963.

34 P. Ayotte, G. H. Weddle, J. Kim and M. A. Johnson, *J. Am. Chem. Soc.*, 1998, **120**, 12361.

35 P. J. Marinelli and R. R. Squires, *J. Am. Chem. Soc.*, 1989, **111**, 4101.

36 (*a*) N. F. Dalleska, K. Honma, L. S. Sunderlin and P. B. Armentrout, *J. Am. Chem. Soc.*, 1994, **116**, 3519; (*b*) D. E. Clemmer, Y.-M. Chen, N. Aristov and P. B. Armentrout, *J. Phys. Chem.*, 1994, **98**, 7538.

37 (*a*) A. Irigoras, J. E. Fowler and J. M. Ugalde, *J. Am. Chem. Soc.*, 1999, **121**, 574; (*b*) A. Irigoras, J. E. Fowler and J. M. Ugalde, *J. Am. Chem. Soc.*, 1999, **121**, 8549.

38 D. L. Lessen and P. J. Brucat, *J. Chem. Phys.*, 1989, **91**, 4522.

39 G. Gregoire, N. R. Brinkmann, D. v. Heijnsbergen, H. F. Schaefer and M. A. Duncan, *J. Phys. Chem. A*, 2003, **107**, 218.

40 G. Gregoire and M. A. Duncan, *J. Chem. Phys.*, 2002, **117**, 2120.

41 R. S. Walters, N. R. Brinkmann, H. F. Schaefer and M. A. Duncan, *J. Phys. Chem. A*, 2003, **107**, 7396.

42 (*a*) N. R. Walker, R. S. Walters, G. A. Grieves and M. A. Duncan, *J. Chem. Phys.*, 2004, **121**, 10498; (*b*) N. R. Walker, G. A. Grieves, R. S. Walters and M. A. Duncan, *Chem. Phys. Lett.*, 2003, **380**, 230.

43 J. B. Jaeger, T. D. Jaeger, N. R. Brinkmann, H. F. Schaefer and M. A. Duncan, *Can. J. Chem.*, 2004, **82**, 934.

44 (*a*) G. T. Fraser, A. S. Pine, W. J. Lafferty and R. E. Miller, *J. Chem. Phys.*, 1987, **87**, 1502; (*b*) T. E. Gough, R. E. Miller and G. Scoles, *J. Phys. Chem.*, 1981, **85**, 4041; (*c*) K. W. Jucks, Z. S. Huang, D. Dayton, R. E. Miller and W. J. Lafferty, *J. Chem. Phys.*, 1987, **86**, 4341; (*d*) K. W. Jucks, Z. S. Huang, R. E. Miller, G. T. Fraser, A. S. Pine and W. J. Lafferty, *J. Chem. Phys.*, 1988, **88**, 2185.

45 J. S. Muenter, *J. Chem. Phys.*, 1991, **94**, 2781.

46 M. A. Walsh, T. H. England, T. R. Dyke and B. J. Howard, *Chem. Phys. Lett.*, 1985, **120**, 313.

47 M. J. Weida, J. M. Spherhac and D. Nesbitt, *J. Chem. Phys.*, 1995, **103**, 7685.

48 (*a*) T. D. Vaden, B. Forinash and J. M. Lisy, *J. Chem. Phys.*, 2002, **117**, 4628; (*b*) T. D. Vaden, C. J. Weinheimer and J. M. Lisy, *J. Chem. Phys.*, 2004, **121**, 3102.

49 M. J. Elrod, D. W. Steyert and R. J. Saykally, *J. Chem. Phys.*, 1991, **95**, 3182.

50 R. N. Zare, *Science*, 1998, **279**, 1875.

51 (*a*) F. F. Crim, *Annu. Rev. Phys. Chem.*, 1993, **44**, 397; (*b*) S. S. Brown, H. L. Berghout and F. F. Crim, *J. Chem. Phys.*, 1997, **107**, 8985.

52 A. Irigoras, J. E. Fowler and J. M. Ugalde, *J. Am. Chem. Soc.*, 1999, **121**, 574.

53 R. S. Walters and M. A. Duncan, *Aust. J. Chem.*, 2004, **57**, 1145.

54 (*a*) Y. Inokuchi, K. Ohshimo, F. Misaizu and N. Nishi, *Chem. Phys. Lett.*, 2004, **390**, 140; (*b*) Y. Inokuchi, K. Ohshimo, F. Misaizu and N. Nishi, *J. Phys. Chem. A*, 2004, **108**, 5034.

55 C. W. Bauschlicher Jr, M. Sodupe and H. Partridge, *J. Chem. Phys.*, 1992, **96**, 4463.

56 K. F. Willey, C. S. Yeh, D. L. Robbins, J. S. Pilgrim and M. A. Duncan, *J. Chem. Phys.*, 1992, **97**, 8886.

57 K. Ohashi, K. Terabaru, Y. Inokuchi, Y. Mune, H. Machinaga, N. Nishi and H. Sekiya, *Chem. Phys. Lett.*, 2004, **393**, 264.

58 H. Machinaga, K. Ohashi, Y. Inokuchi, K. N. Nishi and H. Sekiya, *Chem. Phys. Lett.*, 2004, **391**, 85.

59 R. S. Walters, T. D. Jaeger and M. A. Duncan, *J. Phys. Chem. A*, 2002, **106**, 10482.

60 R. S. Walters, P. R. v. Schleyer, C. Corminboeuf and M. A. Duncan, *J. Am. Chem. Soc.*, 2005, **127**, 1100.

61 (*a*) D. v. Heijnsbergen, T. D. Jaeger, G. v. Helden, G. Meijer and M. A. Duncan, *Chem. Phys. Lett.*, 2002, **364**, 345; (*b*) T. D. Jaeger, D. v. Heijnsbergen, S. J. Klippenstein, G. v. Helden, G. Meijer and M. A. Duncan, *J. Am. Chem. Soc.*, 2004, **126**, 10981.

62 J. B. Jaeger, E. D. Pillai, T. D. Jaeger and M. A. Duncan, *J. Phys. Chem. A*, 2005, **109**, 2801.

63 T. D. Jaeger, E. D. Pillai and M. A. Duncan, *J. Phys. Chem. A*, 2004, **108**, 6605.

64 T. D. Jaeger and M. A. Duncan, *J. Phys. Chem. A*, 2005, **109**, 3311.

65 E. D. Pillai, T. D. Jaeger and M. A. Duncan, *J. Phys. Chem. A*, 2005, **109**, 3521.

66 C. J. Weinheimer and J. M. Lisy, *Chem. Phys.*, 1998, **239**, 357.

67 (*a*) O. M. Cabarcos, C. J. Weinheimer and J. M. Lisy, *J. Chem. Phys.*, 1999, **110**, 8429; (*b*) O. M. Cabarcos, C. J. Weinheimer and J. M. Lisy, *J. Chem. Phys.*, 1998, **108**, 5151.

68 (*a*) G. N. Patwari and J. M. Lisy, *J. Phys. Chem. A*, 2003, **107**, 9496; (*b*) G. N. Patwari and J. M. Lisy, *J. Chem. Phys.*, 2003, **118**, 8555.

69 T. D. Vaden and J. M. Lisy, *J. Phys. Chem. A*, 2005, **109**, 3880.

70 M. Gerhards, C. Unterberg and A. Gerlach, *Phys. Chem. Chem. Phys.*, 2002, **4**, 5563.

71 J. M. Headrick, E. G. Diken, R. S. Walters, N. I. Hammer, R. A. Christie, J. Cui, E. M. Myshakin, M. A. Duncan, M. A. Johnson and K. D. Jordan, *Science*, 2005, **308**, 1765.