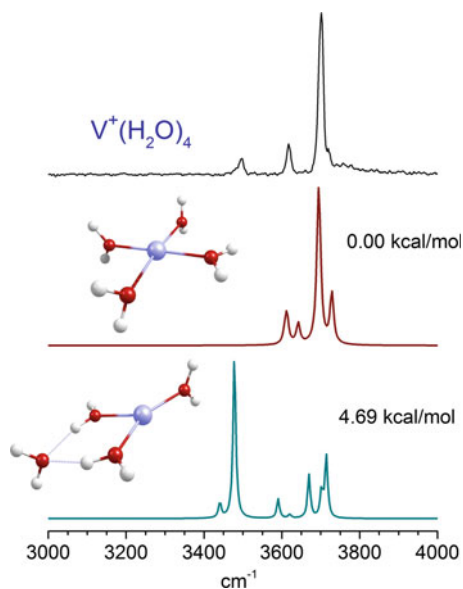


# Chapter 6

## Metal Cation Coordination and Solvation Studied with Infrared Spectroscopy in the Gas Phase



Michael A. Duncan



Metal ion complex infrared spectroscopy and theory to determine structures and coordination numbers

**Abstract** Transition metal cation–molecular complexes are produced in the gas phase environment of a molecular beam using laser ablation in a supersonic expansion. Complexes with carbon monoxide, carbon dioxide, water, acetylene, or benzene are produced by entraining small partial pressures of these molecules into an expansion of either argon or helium. A specially designed time-of-flight mass spectrometer is used to analyze the ions produced and to mass-select them for spectroscopy. Mass-selected ions are excited in the infrared region of the spectrum with a tunable IR optical parametric oscillator laser system to measure photodissociation spectroscopy in the 2000–4500  $\text{cm}^{-1}$  region. Infrared band patterns, combined with structures and spectra predicted by density functional theory, reveal the coordination and solvation interactions in these systems, and how binding to metal distorts the structures of small molecules.

**Keywords** Ion–molecule complexes · Mass spectrometry · Ion spectroscopy · Photodissociation

## 6.1 Introduction

Metal–molecular interactions lie at the heart of heterogeneous [1–5] and homogeneous [6, 7] catalysis, metal–ligand bonding [7–11], metal ion solvation [12–14], metal chelation and sequestration [15], and the function of many biological systems [16]. Additionally, new composite materials, such as metal-decorated nanotubes, metal-intercalated graphene, or metal-organic frameworks (MOFs), involve many of the same metal–molecular interactions [17–26]. These areas are critically important in petroleum processing, solar energy generation, hydrogen storage, battery materials, and related areas such as water splitting,  $\text{CO}_2$  reduction, or heavy metal waste disposal. However, the molecular-level understanding of such systems is limited because of the complexity of metal electronic structure and bonding. Conventional chemistry has documented the properties of stable metal complexes and compounds [7–11]. Likewise, heterogeneous catalysis has been studied extensively on well-characterized metal surfaces [1–3]. However, emerging catalytic systems often involve oxide-supported clusters in the ultra-small size range, with a distribution of particle sizes [4, 5, 27–32]. Homogeneous catalysis is mediated by metal complexes in solution with a delicate relationship between coordination and solvation [33–36]. Metal-organic and metal-carbon materials involve cation– $\pi$  interactions [17–19], and metal ion solvation involves many subtleties of covalent versus electrostatic interactions [37–43]. Unfortunately, detailed insights into this rich and varied chemistry are often limited because theory and experiments cannot study the same systems in the same environment. Isolated metal complexes provide model systems, more tractable for theory, that can elucidate key interactions. Careful investigations of elec-

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tronic structure, geometries, bonding energies, and reactivity are therefore possible. As discussed in this chapter, our research focuses on these model metal–molecular complexes and their clusters using molecular beam sources, mass spectrometers, and infrared laser spectroscopy, in combination with computational chemistry.

To investigate metal systems containing a specific composition, we study *ionized* clusters and complexes which can be mass-selected. Isolated metal centers or those with specific numbers of attached ligand or solvent molecules can be produced and studied. Transition metal ion–molecule complexes have been studied with mass spectrometry for many years, providing reaction products and rates, as well as bond energies [44–57]. While these data are valuable, *spectroscopy* is needed on these systems, evaluated with corresponding computational studies, to make real progress in the understanding of metal electronic structure and bonding.

Vibrational spectroscopy provides the best probe of structure and bonding for metal complexes, and both IR and Raman spectroscopy have been used for many years in this area [58, 59]. However, although these methods are straightforward for conventional inorganic complexes [58], and can be adapted for adsorbates on surfaces [59], they are not easily applied to low-density samples in the gas phase. Vibrational information can be obtained via electronic [60–81] or photoelectron spectroscopy [82–97], but IR spectra can be compared more directly to the predictions of theory. Small metal ions have been studied with infrared absorption spectroscopy in rare gas matrices [98], but the identification of the spectral carrier in these experiments can be ambiguous. Ionized complexes in the gas phase can be size-selected with mass spectrometers, but the resulting density is too low for absorption spectroscopy. Ion spectroscopy is often further complicated by the conditions in ion sources, generally involving discharges, hot plasmas, or other forms of energetic excitation. Until recently, these issues severely limited the IR spectroscopy of ions. However, much recent progress has been made in this area [99–118]. Improved ion sources using laser ablation or electrospray ionization (ESI) now produce a wide variety of metal–ligand and metal–solvent complexes. Ion cooling, needed for sharp spectra, has been implemented with supersonic expansions or cryogenic ion traps. Sensitivity limitations have been addressed by using laser photodissociation spectroscopy rather than absorption. Finally, new IR lasers provide intense sources with broad tuning ranges to access the full-vibrational spectrum [119, 120]. Infrared spectroscopy of gas phase ions is now a rapidly expanding area of research, in which our group has been actively engaged.

Our experiments use laser vaporization in pulsed-nozzle/supersonic molecular beam sources to produce cold metal-containing ions [121]. Although other groups use electrospray ionization (ESI) sources, we find the laser source to be better suited to the ions we study. The ions produced are analyzed and mass-selected with a specially designed reflectron time-of-flight spectrometer (RTOF) [122]. This instrument provides high throughput for maximized ion density, while maintaining the cold temperatures produced by the source. The selected ions are spatially bunched at the turning point in the reflectron field to optimize overlap with the laser. Excitation here allows the full mass spectrum to be detected for each laser shot so that different fragment channels can be recorded simultaneously. The experiment uses the high-intensity,

broadly tunable, optical parametric oscillator/amplifier (OPO/OPA) laser sold by LaserVision [119]. Its main configuration covers the range of 2000–4500  $\text{cm}^{-1}$ , corresponding to the higher frequency vibrations of small ligand or solvent molecules. A second OPA configuration uses silver-gallium-selenide crystals, extending the tuning range to the 600–2300  $\text{cm}^{-1}$  region [120]. Here, we study lower frequency ligand or solvent vibrations, as well as the M–O stretches of oxide clusters. The two laser configurations allow almost full coverage of the infrared spectrum. Combined with our ion source and mass spectrometer, these lasers have produced spectroscopy for many transition metal–molecular complexes [106, 107, 123–169]. This work is complemented by that of other groups using similar infrared OPO laser systems [108–118, 170–200] or free-electron lasers (FELs) [201–212].

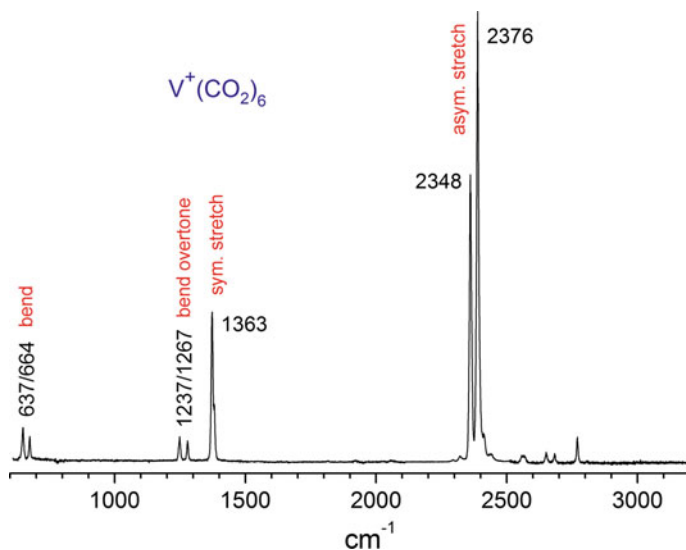
This kind of mass spectrometry combined with IR spectroscopy provides the coordination numbers, geometries and electronic structures of metal–molecular complexes. Mass spectra and photodissociation patterns reveal the number of ligand or solvent molecules attached to a specific metal center. The vibrations in these complexes typically occur near those of the corresponding free ligand or solvent molecules, indicating that binding usually takes place without dissociation or insertion chemistry. The number of IR bands, their shifts compared to the vibrations of the isolated ligand or solvent molecules, and the relative band intensities provide distinctive patterns that can be compared with the predictions of theory to determine structures. Density functional theory (DFT) is used in these studies, although we use due caution in its applications. For example, a well-known issue in transition metal complexes is determination of the correct spin configuration giving rise to the ground state [213–219]. DFT has trouble with the relative energies of spin states, but usually predicts a valid infrared pattern for each spin state. The measured vibrational patterns are then compared with the (scaled harmonic) predictions of theory for different electronic states. These vibrational patterns, rather than the computed relative energies, are generally good enough to determine the spin of the ground state or to reveal the presence of more than one electronic state. Infrared patterns can also reveal the occurrence of intracluster reactions through the appearance of new spectra corresponding to reaction products.

A key aspect of this work is the ligand or solvent molecule binding energy and our ability to cause fragmentation with IR photons. Dissociation energies for many metal ion complexes are known via methods such as collision-induced dissociation [44–55]. Bond energies range from 5000  $\text{cm}^{-1}$  (12–15 kcal/mol) for electrostatically bonded metal– $\text{CO}_2$  ions, up to as high as 30,000  $\text{cm}^{-1}$  (70–80 kcal/mol) for metal–benzene complexes with strong covalent bonds. Across this range, one photon infrared excitation on vibrational fundamentals is not energetic enough to cause photodissociation. Bond energies usually decrease in complexes with more ligands, but these systems have the same problem until the metal coordination is completed. However, when ligands are present beyond the inner-sphere coordination, they are bound by weaker electrostatic forces and their elimination is efficient, providing good spectra. The onset of greater dissociation yields therefore identifies the coordination number. To study smaller complexes with partial coordination and stronger bonding, we attach weakly bound rare gas atoms, using the “tagging” method first

used by Lee et al. [99–101]. This general method is now used throughout ion spectroscopy [102–118]. To document the effects of tagging, we use theory to investigate the spectra of complexes with and without the tag atom.

Another essential requirement for this work has been the extension of IR laser coverage to the fingerprint region. In the past, this could only be done using FEL's, such as the FELIX system in the Netherlands. Previous studies there by our group and others used infrared resonance-enhanced *multiphoton* dissociation (IR-REMPD) of cations to obtain vibrational spectra [201–212]. However, the quality of these spectra is often poor because of the laser line width and power broadening from the multiphoton processes. The new OPO's have broader wavelength coverage ( $600\text{--}4500\text{ cm}^{-1}$ ) and higher resolution. Using tagging, or elimination of external ligands, spectra can be measured via *single-photon* dissociation, and line widths are much improved ( $1\text{--}5\text{ cm}^{-1}$ , limited by predissociation). As shown in Fig. 6.1, the quality of the spectra obtained is excellent.

In this chapter, we describe the work from our lab investigating metal ion complexes with carbon monoxide [143–155], carbon dioxide [123–128], water [129–142], acetylene [156–162], and benzene [165–168]. These experiments show that IR photodissociation spectroscopy can be applied to ions containing virtually any metal or ligand. It provides the dissociation products, the number of IR-active vibrations, the frequency shifts that occur when ligands bind to metal, and the rela-



**Fig. 6.1** The infrared spectra of  $V^+(CO_2)_6$  complexes, illustrating the broad tunability of our IR-OPO lasers. The  $CO_2$  bend and asymmetric stretch have two bands corresponding respectively to molecules coordinated to the metal ion and those attached only to other  $CO_2$  molecules. The symmetric stretch is only IR-active for molecules attached to the metal and a single band is observed here

tive intensities of different bands. Computational chemistry complements the experiments, predicting the structures of complexes, their electronic configurations, and their spectra.

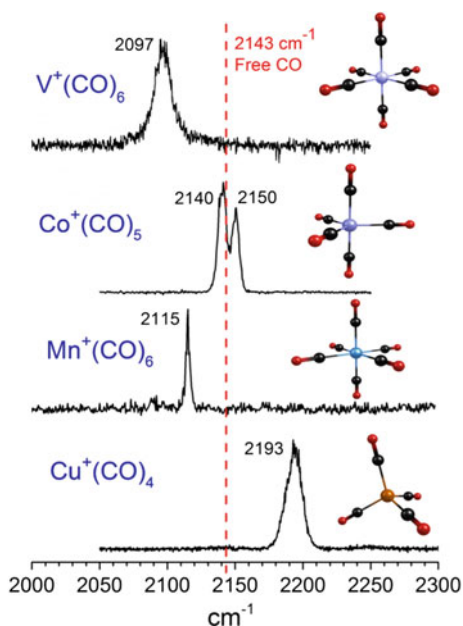
## 6.2 Metal-Carbonyl Complexes

Transition metal carbonyls provide classic examples of inorganic complexes [7–11], and CO is the classic probe molecule for surface science and catalysis [1–3, 58]. In both contexts, the carbonyl stretch reveals the nature of the bonding. Metal carbonyls are characterized by the positions of the C–O stretch relative to the vibration of the isolated CO diatomic ( $2143\text{ cm}^{-1}$ ) [220]. Unsaturated carbonyls, including ions, have been investigated by mass spectrometry [45–55, 221–226], matrix isolation spectroscopy [98], and photoelectron spectroscopy [82, 83, 85, 87]. Computational studies have explored the mechanism of the shifts that occur for the C–O stretches in different systems, including the familiar effects of  $\sigma$  donation and  $\pi$  back-bonding [219, 227–235]. Our group has investigated transition metal carbonyl cations [143–155] to compare these to well-known neutrals. Other research groups have used similar methods to investigate other atomic metal cation–carbonyls [190–197] or the carbonyls of metal atom clusters [205–209].

We first studied cation complexes that could provide isoelectronic analogs to known neutral metal carbonyl complexes. The  $\text{Co}^+(\text{CO})_5$  complex provided an analog to  $\text{Fe}(\text{CO})_5$  [145],  $\text{Mn}^+(\text{CO})_6$  provided an analog to  $\text{Cr}(\text{CO})_6$  [147], and  $\text{Cu}^+(\text{CO})_4$  provided an analog to  $\text{Ni}(\text{CO})_4$  [150]. In each case, the cations were found to have the same coordination and structures as the corresponding neutrals (trigonal pyramid, octahedral, and tetrahedral, respectively) and the same closed-shell singlet ground states. However, significant differences were apparent in the spectroscopy between the neutrals and the corresponding cations. In the neutrals, the C–O stretch vibrations are strongly red-shifted compared to the stretch of molecular CO by  $100\text{--}150\text{ cm}^{-1}$ . However, as shown in Fig. 6.2, the C–O stretch vibrations were hardly shifted at all for the Co and Mn cations and they were *blue*-shifted for the Cu cations. The frequencies for these neutrals and ions are summarized in Table 6.1. It is well known in inorganic chemistry that the shifts of the C–O stretches arise from the competing effects of  $\sigma$  donation and  $\pi$  back-bonding [219, 227–235]. For most neutral metals,  $\pi$  back-bonding is the more significant factor, and the carbonyl stretches occur at much lower frequencies than that of CO itself. The smaller red shifts seen for the cations here are attributed to their reduced  $\pi$  back-bonding [149]. Blue shifts to higher frequencies are known to occur for certain metals with filled *d* shells that are inefficient at back donation. We find this behavior not only for the copper carbonyl cations shown here [150], but also for  $\text{Au}^+$ ,  $\text{Pt}^+$  and  $\text{Rh}^+$  carbonyl complexes [143, 144, 155].

The fully coordinated ions and their corresponding neutrals shown in Table 6.1 all have the 18-electron configuration, which is recognized as a guiding principle in transition metal chemistry. We were also interested to see how robust this rule

**Fig. 6.2** The infrared spectra of the saturated carbonyl complexes for selected metal cations. The red dashed line shows the frequency of the isolated CO molecule

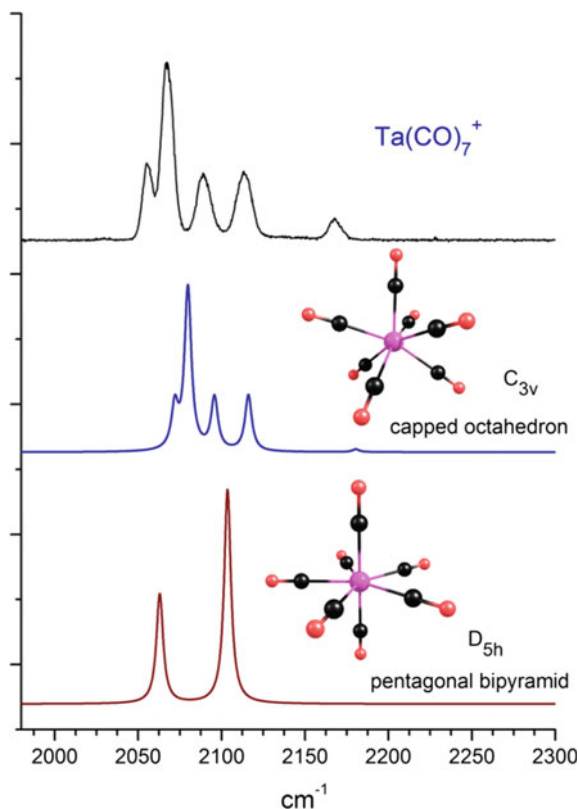


**Table 6.1** A comparison of the carbonyl stretch frequencies for isoelectronic neutral and cationic complexes

Complex	Experimental C–O stretch (cm <sup>-1</sup> )
Cr(CO) <sub>6</sub>	2003 [236]
Mn <sup>+</sup> (CO) <sub>6</sub>	2115
Fe(CO) <sub>5</sub>	2013, 2034 [237]
Co <sup>+</sup> (CO) <sub>5</sub>	2140, 2150
Ni(CO) <sub>4</sub>	2056 [238]
Cu <sup>+</sup> (CO) <sub>4</sub>	2193

is, and what its limitations are, if any. Early transition metals have fewer valence *d* electrons, and therefore would require more carbonyl ligands to achieve the 18-electron configuration. We investigated the cation carbonyls of the group V metals (V, Nb, Ta) [146, 151], which would need seven carbonyls to reach this limit, and those of Sc and Y [154], which would need eight carbonyls, to see if such higher coordination numbers were possible. According to theory, these higher coordination complexes are stable for each of these metals. However, we found experimentally that vanadium did not form the seven-coordinate (7C) carbonyl, but instead formed the six-coordinate (6C) complex (see spectrum in Fig. 6.2). Niobium and tantalum, on the other hand, did form the 7C complexes. The spectrum of Ta<sup>+</sup>(CO)<sub>7</sub>, which forms a capped octahedral structure rather than the pentagonal bipyramid, is presented in Fig. 6.3. Likewise, scandium did not form the 8C complex, but yttrium did. In both groups, only the heavier metals formed the expected high coordination. We explained

**Fig. 6.3** The infrared spectrum of  $\text{Ta}^+(\text{CO})_7$  compared to the spectra predicted by density functional theory for two different isomers. The spectrum agrees with that predicted for the capped octahedron structure



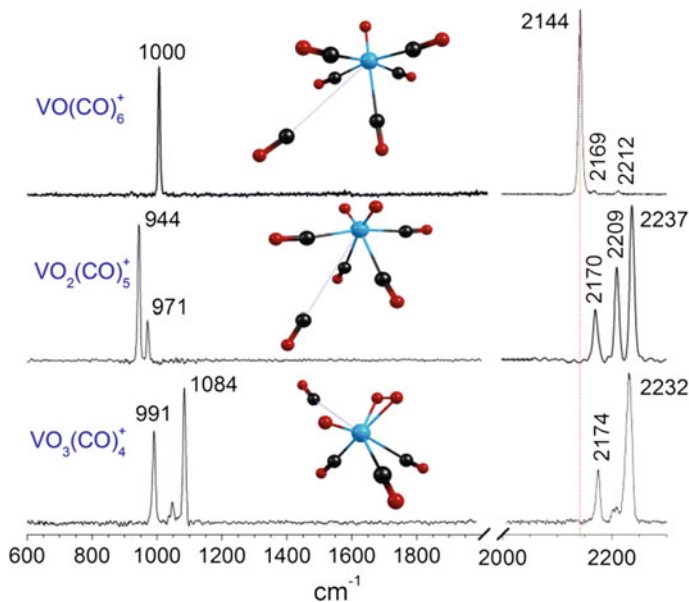
this trend in terms of the kinetics of carbonyl addition to these metals. In both systems, the filled coordination produces a singlet ground state, while the  $n - 1$  complex is a triplet. Adding the last CO therefore requires a spin change, which may inhibit the rate of this process. Our clusters grow in a 1–3 ms time frame (defined by the pulsed jet expansion) by sequential addition of ligands to the ablated metal cations, and therefore slower growth rates may inhibit the formation of complexes, even if they are stable. The heavier metals with stronger spin-orbit coupling should change spin more readily, possibly explaining how these species could achieve the higher coordination. This reasoning was used previously by Weitz et al. to explain similar results for CO addition to unsaturated neutral carbonyls [239, 240]. Harvey et al. used computational studies to model these spin-controlled kinetics [241–243]. Since our work on these systems, Zhou and coworkers have found eight-coordinate complexes for other early transition metal cations [196], and they have found unexpected 8C complexes for the alkaline earth metal cations [197].

The group IV metals (Ti, Zr, Hf) all have an odd number of electrons as cations, and it is therefore unclear what coordination would be expected for these systems. We found that they all formed 6C complexes rather than the 7C (17-electron) or 8C (19-electron) species [152, 195]. Rhodium carbonyls provided another interesting



case [155].  $\text{Rh}^+$  is a  $d^8$  species, which is generally expected to form 4C square planar complexes [11], even though the 18-electron species would be 5C. We found a primary coordination of four carbonyls but a secondary coordination of five. The fifth ligand had an intermediate binding energy, weaker than the first four, but not as weak as the external ligands. The spectrum of the  $n = 4$  complex indicated a square-planar structure, while that of the  $n = 5$  species was a square pyramid.

We have also studied metal oxide carbonyls. Oxidation of the metal center removes the  $d$  electron density available for back-bonding, which reduces or eliminates the red shifts in these systems. The  $\text{V}^+(\text{CO})_6$  complex spectrum has a slightly red-shifted C–O stretch, with one main band because of the octahedral structure [146, 151].  $\text{VO}^+(\text{CO})_5$ ,  $\text{VO}_2(\text{CO})_4^+$ , and  $\text{VO}_3(\text{CO})_3^+$  (each measured by elimination of one excess CO from the next larger complex) have C–O stretches shifted progressively further to the blue because of the reduced back-bonding (Fig. 6.4) [153]. Similar blue-shifted carbonyl stretches are observed for CO binding on metal oxide surfaces [2, 59]. The metal–oxygen stretches in these clusters can be compared with those of the corresponding  $\text{VO}^+$ ,  $\text{VO}_2^+$ , and  $\text{VO}_3^+$  ions recently measured by Asmis et al. [244]. The oxide stretches in the carbonyls shift to the red compared to those in the isolated oxides, another result of partial charge transfer in these systems.

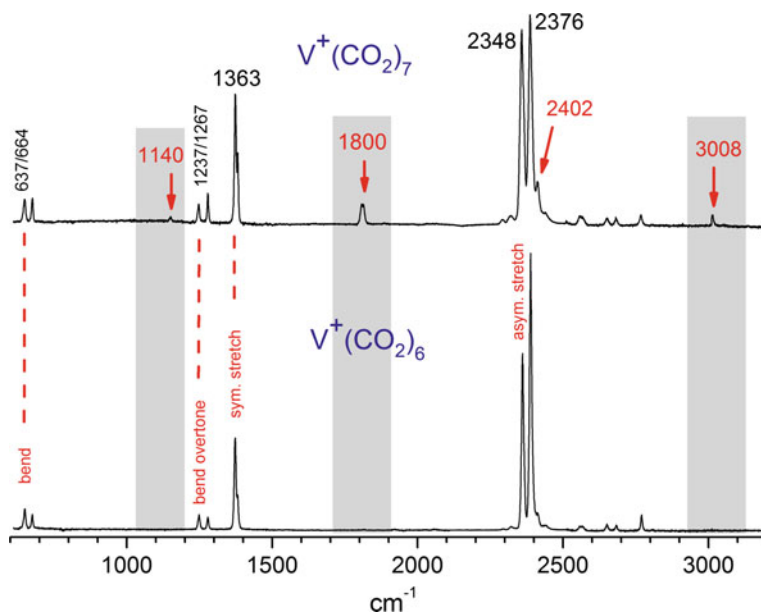


**Fig. 6.4** The IR spectra of vanadium oxide carbonyls and the structures predicted to be most stable for these complexes. Each complex has one external ligand, which is eliminated in the photodissociation process to obtain the spectrum. The C–O stretch vibrations are shifted to the same or higher frequencies than the free-CO vibration, indicated as the dashed red line. The bands at 2169–2174  $\text{cm}^{-1}$  come from the external CO ligand

### 6.3 Metal–CO<sub>2</sub> Complexes

The binding of CO<sub>2</sub> to metals is of widespread importance for CO<sub>2</sub> capture and catalytic conversion to small organics [20, 21, 25, 34, 35]. However, the binding of CO<sub>2</sub> to metal ions in the gas phase involves primarily electrostatic interactions [245–247], and these systems have been studied less than the corresponding carbonyl complexes. Our lab has studied the electronic spectroscopy of Mg<sup>+</sup>(CO<sub>2</sub>) [65] and Ca<sup>+</sup>(CO<sub>2</sub>) [67], and the infrared photodissociation spectroscopy of several M<sup>+</sup>(CO<sub>2</sub>)<sub>n</sub> cation complexes [123–127]. Figure 6.1 shows the infrared spectrum of V<sup>+</sup>(CO<sub>2</sub>)<sub>6</sub>, which illustrates the behavior seen for many of these systems. Of the normal modes for CO<sub>2</sub>, the degenerate bending mode ( $\nu_2$ , 667 cm<sup>-1</sup>) and the asymmetric stretch ( $\nu_3$ , 2349 cm<sup>-1</sup>) are IR active for the isolated molecule, whereas the symmetric stretch ( $\nu_1$ , 1333 cm<sup>-1</sup>) is inactive [248]. However, theory and experiments agree that metal cation binding is most favorable in the M<sup>+</sup>–O=C=O linear configuration. In this structure, all three vibrations are IR active. As shown in the figure, CO<sub>2</sub> molecules attached to metal have these three vibrations, with shifts to higher frequencies than the vibrations of the isolated molecule. In a cluster like V<sup>+</sup>(CO<sub>2</sub>)<sub>6</sub>, there are coordinated molecules, which give rise to shifted vibrations, and second-sphere molecules not attached to the metal whose vibrations are mostly unshifted. This gives rise to doublet features (shifted plus unshifted bands) for the asymmetric stretch and bending vibrations, and a single band (shifted only) for the symmetric stretch, which is only IR-active when it is attached to the metal. This pattern of bands has been seen for almost all the metal ion–CO<sub>2</sub> complexes that we have studied.

An exception to this general behavior occurs in larger V<sup>+</sup>(CO<sub>2</sub>)<sub>n</sub> clusters, in which additional bands were seen beyond the coordination and solvation features. As shown in Fig. 6.5, new bands at 1140, 1800, 2402, and 3008 cm<sup>-1</sup> were seen for clusters with seven or more CO<sub>2</sub> ligands, and these bands became more intense in the larger clusters. These new bands suggest that there was an *intracluster reaction* producing a new kind of structure. Because the clusters were mass-selected, the reaction product must have the same mass as one or more CO<sub>2</sub> units, which could be true for an oxide-carbonyl species, VO<sup>+</sup>(CO)(CO<sub>2</sub>)<sub>n-1</sub>, a metal carbonyl-carboxylate species, V<sup>+</sup>(CO)(CO<sub>2</sub>)<sub>n-1</sub>(CO<sub>3</sub>), or a metal oxylate species, V<sup>+</sup>(CO<sub>2</sub>)<sub>n-2</sub>(C<sub>2</sub>O<sub>4</sub>). To explore these possibilities, we made the oxide-carbonyl species direct, and found that the VO<sup>+</sup> and carbonyl stretches in these systems (Fig. 6.4) do not match the new bands. Instead, we found that the reaction product is an oxalate species (C<sub>2</sub>O<sub>4</sub><sup>-</sup>), with covalently linked CO<sub>2</sub> molecules. The lower frequency vibrations (1140 and 1800 cm<sup>-1</sup>) are those of the oxalate moiety, and the higher frequency vibrations (2402 and 3008 cm<sup>-1</sup>) are those of solvating CO<sub>2</sub> molecules interacting with the new kind of charge center in the clusters. Although we cannot determine the exact charge states in this system, oxalate is most stable when it carries a negative charge. This reaction therefore apparently occurs by electron transfer from the V<sup>+</sup> ion to CO<sub>2</sub>, producing a V<sup>2+</sup>, C<sub>2</sub>O<sub>4</sub><sup>-</sup> ion pair. This suggestion would explain the onset at larger cluster sizes. Solvation from the surrounding excess CO<sub>2</sub> molecules could stabilize the higher charge state of V<sup>2+</sup> and that of the oxalate. Theory on this system is plagued



**Fig. 6.5** The infrared spectrum of  $\text{V}^+(\text{CO}_2)_7$  compared to that for  $\text{V}^+(\text{CO}_2)_6$  showing the sudden appearance of several new vibrations associated with an intracuster reaction

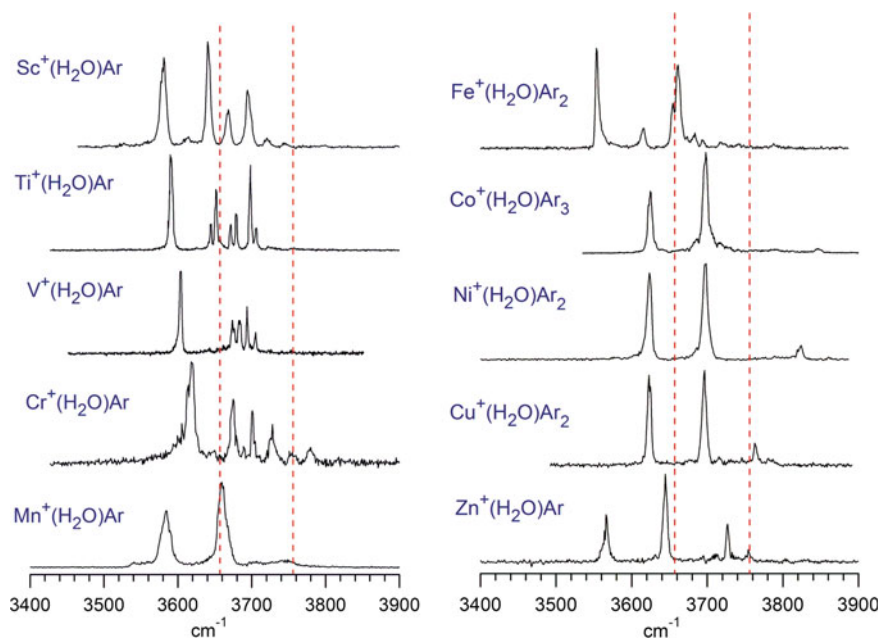
by multireference issues, and we were not able to determine whether the ion pair is in contact or solvent-separated. However, the same kind of chemistry has also been seen by Weber and coworkers [174] for negative ion  $\text{M}^-(\text{CO}_2)_n$  clusters. Apparently, the negative charge on  $\text{CO}_2$  activates it to enable a rich variety of chemistry.

## 6.4 Metal–Water Complexes

The interaction of water with metal ions is fundamental to the chemistry of solvation [12–14, 37–43]. Unfortunately, the details of cation–water interactions are difficult to obtain from solution measurements, which involve ensemble averaging over many structures. Gas phase measurements have investigated the thermochemistry of cation–water bonding [47, 48, 50, 54, 55, 249–264], and computational studies have studied structures and energetics of these systems [57, 265–277]. However, infrared spectroscopy probes the structures of these systems more directly. Our work has examined several  $\text{M}^+(\text{H}_2\text{O})_n$  and  $\text{M}^{2+}(\text{H}_2\text{O})_n$  systems [129–142], focusing on both the mono-hydrated complexes and the coordination behavior when multiple water molecules condense around the metal ion. Other groups have also explored the same kinds of systems using similar methods [170–173, 178–181, 183–187, 192].

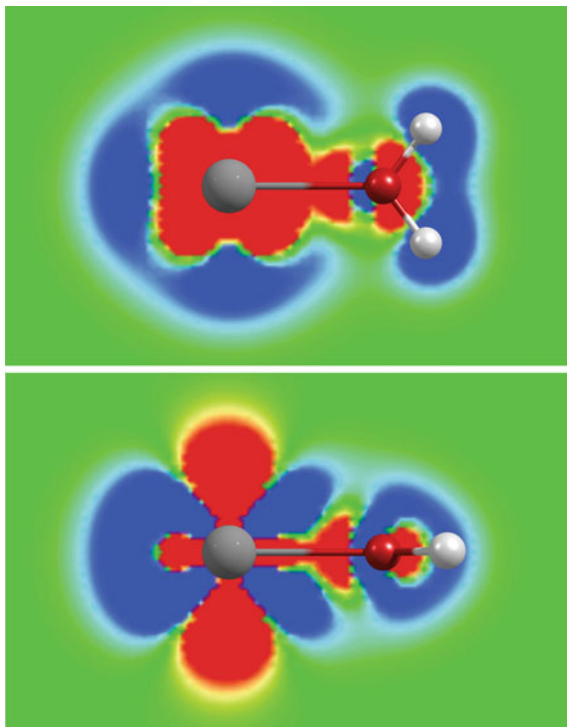
We have studied nearly all of the singly charged first-row transition metals in complexes with a single water molecule [129–142]. The spectra in the O–H stretching

region are shown in Fig. 6.6. The binding energies of argon are very different for the early versus late transition metals. Consequently, the late transition metals require the attachment of two or more argon atoms before photodissociation can be measured in this region of the IR. As shown in the left frame of the figure, those complexes tagged with a single argon have more complex vibrational patterns than those tagged with two argons. The additional structure at higher frequency arises from partially resolved rotational structure (K-type bands) on the asymmetric stretch band. This structure is discussed in more detail later. We found that water bound to metal ions generally has O–H stretching frequencies that are shifted to the red compared to those of the free molecule (3657 and 3756  $\text{cm}^{-1}$  for the symmetric and asymmetric stretches, respectively) [248]. In a charge-transfer process not unlike that for metal carbonyls, the cation polarizes water, removing electron density from its highest occupied molecular orbital. This orbital involves not only the non-bonding lone pairs on oxygen but also has bonding character along the O–H bonds; weakening these bonds lowers the vibrational frequency. Figure 6.7 shows the electron density map of the  $\text{Ti}^+(\text{H}_2\text{O})$  complex in its doublet ground state compared to that in the separated



**Fig. 6.6** The infrared spectra in the O–H stretching region for different transition metal cation–water complexes compared to the symmetric and asymmetric O–H stretch frequencies for the isolated water molecule (dashed red lines). The early transition metal complexes are tagged with a single argon, producing partially resolved rotational structure in some cases, whereas the late-transition metal complexes are usually tagged with two or three argons. The spectra for the early transition metal complexes are generally shifted further to the red than those of the late transition metals. The lowest frequency band for  $\text{Fe}^+(\text{H}_2\text{O})$  is from an isomer with argon attached to an OH of water, inducing an even greater red shift [130]

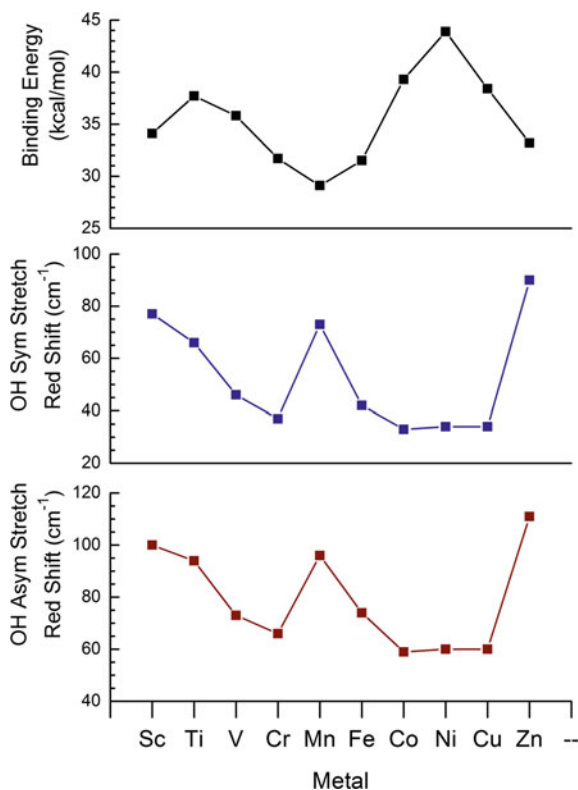
**Fig. 6.7** The charge density map of the  $\text{Ti}^+(\text{H}_2\text{O})$  complex in its doublet ground state. Red color shows an increase in charge density compared to the separated cation–water system, whereas blue shows a reduction in charge density



cation–molecule system. This illustrates the effects of the charge transfer between the water and the metal. As shown in the two views, electron density increases on the metal ion center, and decreases in the vicinity of the O–H bonds. This charge transfer drives the shift in the vibrational frequencies. In addition to the red shift in the frequencies—which varies considerably with different metals—the relative intensities of the two O–H stretches change, with the symmetric stretch gaining relative to the asymmetric. In the free water molecule, the asymmetric/symmetric stretch intensity ratio is about 18:1, whereas in the cation water complexes this ratio is closer to 1:1. The symmetric stretch in these metal complexes oscillates charge more effectively along the molecular axis, enhancing the dynamic dipole and the IR intensity. The shifts seen for these singly charged metal complexes have been compared with selected examples of doubly charged complexes [135, 137–139]. In those systems, the shifts of the vibrational frequencies and the enhancement of the symmetric stretch intensity are both greater than that for the corresponding singly charged complexes.

Interestingly, the shifts of the O–H stretching frequencies measured are generally greater for the early transition metals than they are for the late transition metals. Figure 6.8 shows a plot of the O–H stretch frequencies across the periodic table groups and a comparison to the corresponding  $\text{M}^+(\text{H}_2\text{O})$  bond energies determined in other labs. Surprisingly, the magnitudes of the red shifts for the two O–H stretches

**Fig. 6.8** Plots of the shifts in the O–H stretches for different transition metal cation–water complexes compared to the cation–water binding energies

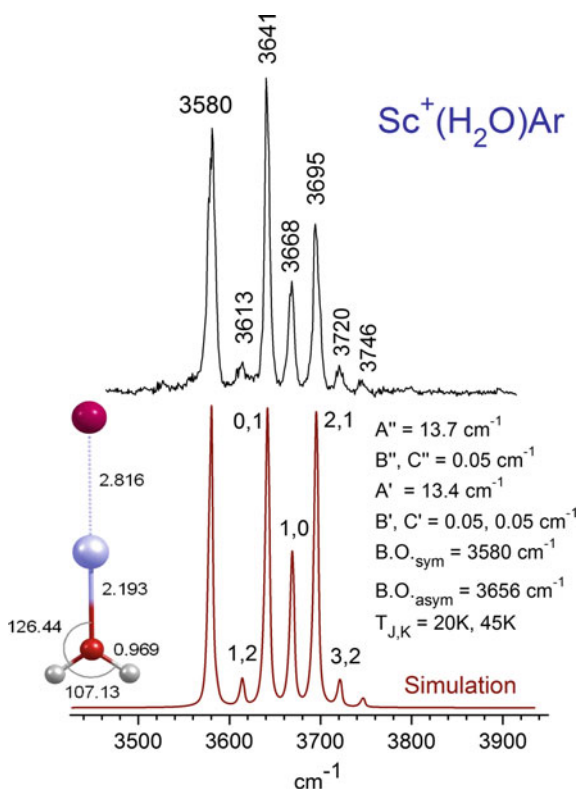


of water are greater for the early transition metal, and less for the late transition metals, with a local maximum for the manganese cation. The binding energies are greater for the late transition metals. It therefore seems that there is no clear correlation between binding energies and vibrational band shifts, even though the charge transfer that causes the vibrational shifts should have at least some relevance for the electrostatic bonding in these systems. However, the bonding in these transition metal–water complexes is a complex mixture of both electrostatic and covalent interactions, and so it may be oversimplified to assume a correlation between these two properties. It is worth noting that density functional theory accurately predicts both the trends in binding energies and vibrational frequency shifts.

In  $\text{Ar-M}^+(\text{H}_2\text{O})$  complexes when the tag atom binds opposite water, the complex has  $C_{2v}$  symmetry and is nearly a symmetric top, with only the light hydrogen atoms located off the  $C_2$  symmetry axis. This causes the  $A$  rotational constant to be relatively large ( $>10 \text{ cm}^{-1}$ ) and K-type rotational sub-band structure can be resolved, even with our modest  $1 \text{ cm}^{-1}$  laser line width. This is apparent in the spectra for the early transition metals, in the left frame of Fig. 6.6, with the exception of the  $\text{Mn}^+(\text{H}_2\text{O})$  spectrum (it binds argon in a bent position, which produces a much smaller  $A$  constant, and the structure is not resolved [138]). In these systems, a multiplet structure arises

for the asymmetric stretch, which is a perpendicular-type band. The symmetric stretch is a parallel-type band, with more closely spaced rotational structure that cannot be resolved under these conditions. Because the hydrogen molecules of water are equivalent by symmetry, *ortho-para* symmetry rules must be applied, resulting in a 3:1 statistical weight for transitions originating in the  $K = 1$  versus  $K = 0$  levels. At low temperature, only the  $K = 0$  and 1 levels are populated significantly, and  $K = 1$  cannot relax to  $K = 0$  because of the nuclear spin symmetry. The only transitions seen are those originating from these two levels. The  $K'' = 0 \rightarrow K' = 1$  transition (labeled 0,1 in the figure) is then lower in relative intensity than the  $K'' = 1 \rightarrow K' = 0$  or  $K'' = 1 \rightarrow K' = 2$  transitions (labeled 0,1 and 2,1 in the figure). The rotational structure can be simulated using the PGopher software [278], and the parameters are adjusted to get the best match with the experiment, as shown in Fig. 6.9. The best fit produces the  $A$  rotational constant and the temperature of the ions. As shown in the figure, the non-equilibrium conditions of the supersonic molecular beam produces slightly different temperatures for the  $J$  and  $K$  quantum states, an effect that is not uncommon in such molecular beam experiments. Assuming that the O–H bond distances remain nearly constant (suggested by theory), then the  $A$  rotational constant reveals the H–O–H angle, which is often expanded by the cation–water polarization interaction. In the scandium example shown here, this angle is estimated to be  $107.13^\circ$ , which is significantly larger than the angle in an isolated water molecule ( $104.7^\circ$ ). Our rotationally resolved studies on the  $\text{Sc}^+$ ,  $\text{Ti}^+$ ,  $\text{V}^+$ ,  $\text{Nb}^+$ , and  $\text{Cr}^+$  systems all found H–O–H angles expanded with respect to that of water [135, 137, 141, 142]. In the case of the vanadium and niobium complexes, the analysis of the rotational structure was complicated by an unexpected quenching of the *ortho-para* separation catalyzed by the metal ions, changing the selection rules and the appearance of the spectra [142].

IR spectroscopy of metal cations solvated by multiple water molecules can reveal their coordination numbers. In small clusters, water coordinated directly to metal has free O–H stretching vibrations near those of the isolated water molecule. However, when water adds to the second sphere, hydrogen bonding causes a strong red shift of  $200\text{--}400\text{ cm}^{-1}$  in the O–H stretches, and the IR intensity increases. The first appearance of vibrations in the hydrogen bonding region therefore identifies the coordination number for the metal cation. We found in the past that this is four water molecules for  $\text{Ni}^+$  [132], and three for  $\text{Zn}^+$  [140]. Figure 6.10 shows spectra for different sizes of  $\text{V}^+(\text{H}_2\text{O})_n$ , in which the first evidence for a band in the hydrogen bonding region occurs for the  $n = 4$  cluster, indicating that the coordination is complete with three molecules [278]. In related work, Nishi et al. studied  $\text{V}^+(\text{H}_2\text{O})_n$  complexes without tagging, finding a coordination of four molecules [172]. Our result here can be rationalized to agree with their result, if we assume that argon acts as a coordinating ligand in at least some of the  $n = 4$  complexes.  $\text{V}^+$  ions exhibited a coordination of six for carbonyl ligands [146, 151] and four for  $\text{CO}_2$  ligands [127], contrasting with the behavior seen here for water. Coordination numbers for the single positive ions we have studied are generally lower than those expected for

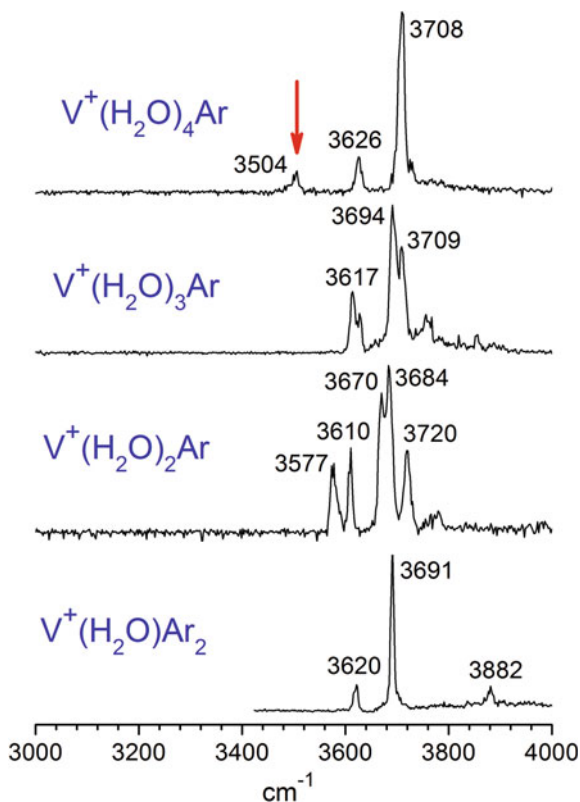


**Fig. 6.9** An expanded view of the IR spectrum in the O–H stretching region for scandium–water cations compared to a simulated spectrum including partially resolved rotational structure. The rotational structure is consistent with expectations for a  $C_{2v}$  structure, with a triplet for the asymmetric stretch and a 3:1 intensity alternation from the nuclear spin statistics. A, B, and C are the rotational constants in the ground (") and excited (') vibrational states, and B.O. indicates the band origins. B and C values come from the theoretical structure, whereas the A values are adjusted to fit the spacings in the spectrum. The temperature is adjusted to fit the relative band intensities ( $T_K$ ) and line widths from unresolved structure ( $T_J$ ) in the spectrum. Figure used from Ref. [137] with permission from the American Institute of Physics, Copyright 2011

the more highly charged metal ions found in normal solutions. The highly charged metal ions in solution have fewer electrons occupying the valence orbitals than the singly charged species. It is likely that ligand–electron repulsion from the occupied orbits causes the lower coordination numbers for the singly charged species.



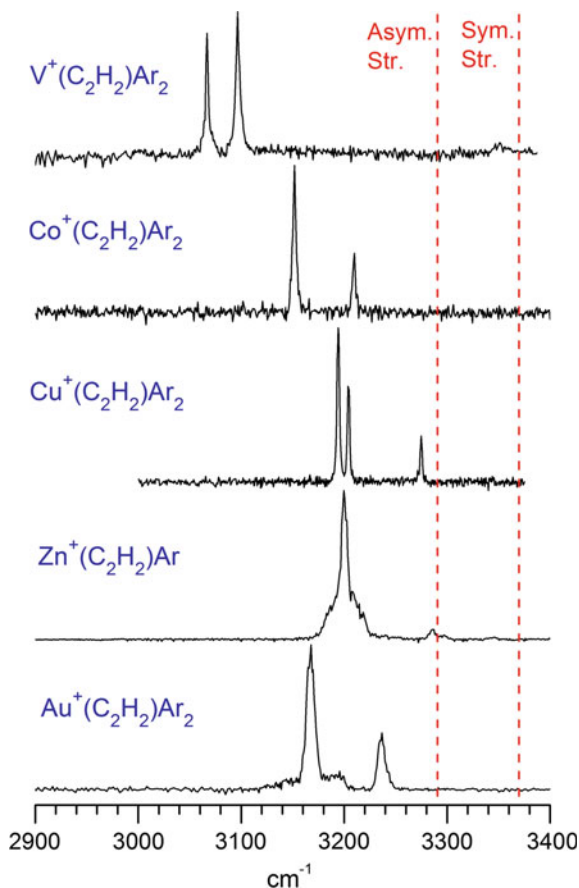
**Fig. 6.10** Infrared spectra for  $V^+(H_2O)_n$  clusters in the  $n = 1-4$  size range. The first evidence for a band in the hydrogen bonding region occurs for the  $n = 4$  cluster, with the band at  $3504\text{ cm}^{-1}$  marked with the red arrow. This suggests that the solvation sphere is filled with the next-smallest  $n = 3$  cluster



## 6.5 Metal–Acetylene Complexes

Metal–acetylene and metal–ethylene complexes form the simplest examples of cation– $\pi$  interactions relevant in many areas of catalysis and biological chemistry [6–11, 16, 279–282]. These systems have been studied often in ion chemistry and investigated with computational chemistry [283–288]. In some of the first spectroscopic work, our group measured electronic spectra for  $Ca^+(C_2H_2)$  and  $Mg^+(C_2H_2)$  complexes [69, 70]. In the infrared, we investigated the C–H stretches in several transition metal ion complexes with a single acetylene [157], comparing the vibrations to the known symmetric and asymmetric stretches of acetylene ( $3374$  and  $3289\text{ cm}^{-1}$ , respectively) [248]. Figure 6.11 shows a comparison of several  $M^+(C_2H_2)$  complexes, including new examples from more recent work. As shown in the figure, all the C–H stretches for these metal ion complexes occur at frequencies lower than those of acetylene itself. The cation– $\pi$  interaction transfers charge from the molecule to the metal in much the same way seen already for metal–carbonyls and metal–water complexes. In acetylene complexes, polarization removes electron density from the C–C and C–H bonds, lowering their frequencies. The C–C and symmetric C–H stretches

**Fig. 6.11** Infrared spectra of cation–acetylene complexes in the C–H stretching region

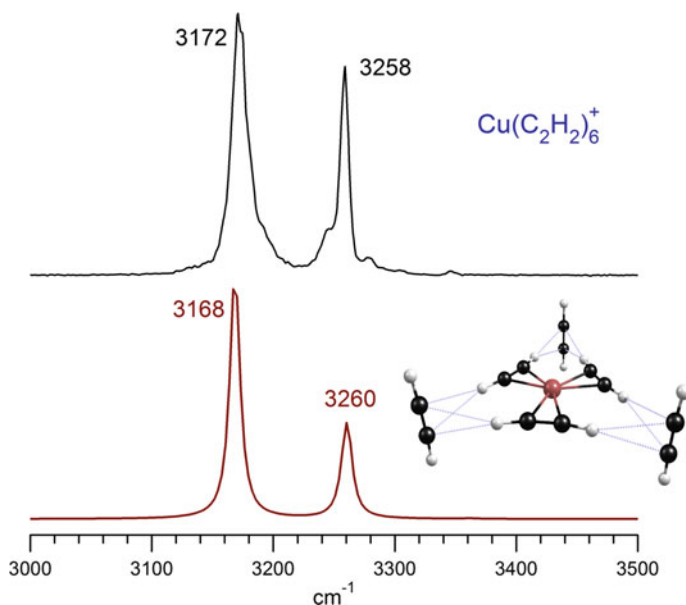


of acetylene are not IR active in the free molecule, whereas the asymmetric C–H stretch is IR-active. However, in cation–acetylene complexes, the C–C and symmetric C–H stretches can become weakly IR active from the distortion of the molecule (e.g., CH groups bending away from linear) or the changing dipole produced by concerted metal and molecular motion. Consequently, the spectra shown in Fig. 6.11 have stronger asymmetric stretch vibrations at lower frequency and weaker symmetric stretch bands at higher frequency. The intensity of the weaker symmetric stretch band varies for different metals depending on the degree of “activation” induced by the metal. The exception to this trend is the  $V^+(C_2H_2)$  complex, which has two bands with nearly equal intensities. This suggests that the bonding in this complex is somehow different from that in the other species considered here.

Computational studies were insightful for these systems. We found that most metals form cation– $\pi$  complexes, with the cation in a two-fold position above the  $\pi$  cloud and some slight bending of the CH groups away from the metal. However, the  $V^+$  complex formed a very different structure—that of a  $VC_2$  *metallacycle* with the

CH groups bent strongly away from the metal (computed CCH angle =  $37.7^\circ$ ). In this bent configuration, both C–H stretches are IR active with comparable intensity and there are much greater red shifts in the two frequencies, all consistent with the experimental spectrum. There are covalent bonds between the metal and the carbons, and the C–C bond has lengthened (computed from 1.199 in acetylene to 1.301 Å in  $V^+$ -acetylene), consistent with its reduced bond order. The interaction between  $V^+$  and acetylene is clearly very different from that of the other metal ions studied so far.

Complexes with multiple acetylene molecules coordinated to a single metal ion make it possible to investigate the coordination sphere and possible reactions between ligands mediated by the metal. In the case of multiple acetylene complexes of  $Ni^+$ , a coordination of four acetylenes was determined in a near-tetrahedral structure [158]. In larger clusters, a new band appeared which indicated an intracuster reaction forming cyclobutadiene [156]. In recent work, we examined the multiple acetylene complexes of  $Cu^+$ , finding an inner coordination of three acetylenes and a secondary solvation of three additional acetylenes in the highly symmetric  $Cu^+(C_2H_2)_6$  complex [159]. In this structure, whose spectrum is shown in Fig. 6.12, each acetylene molecule in the second coordination sphere is bonded to two inner-sphere molecules via bifurcated CH– $\pi$  hydrogen bonds. Because of the highly symmetric structure, the IR spectrum has only two bands corresponding to the in-phase and out-of-phase asymmetric stretches of the core ( $3172\text{ cm}^{-1}$ ) and outer ( $3258\text{ cm}^{-1}$ ) ligands. Gold

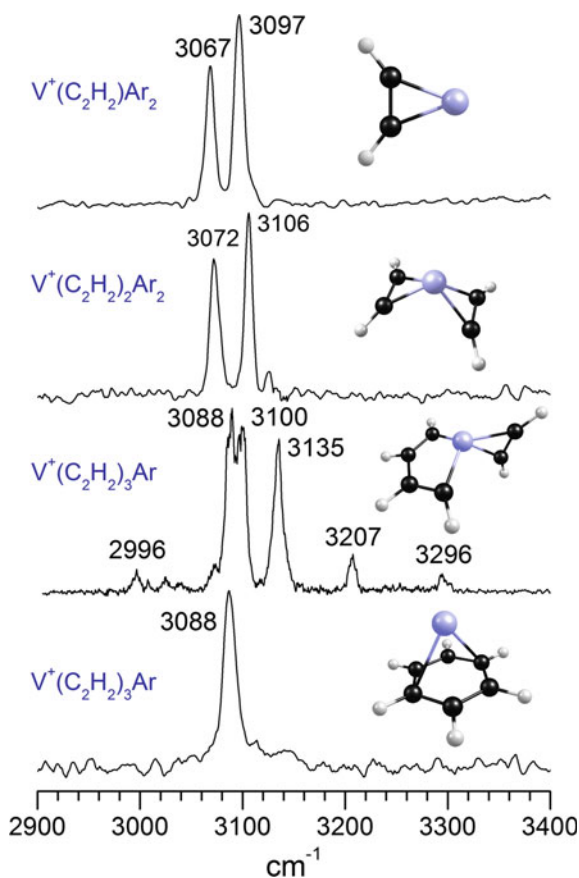


**Fig. 6.12** The infrared spectrum of  $Cu^+(C_2H_2)_6$  and the spectrum predicted by theory for the structure with three inner-sphere and three outer-sphere molecules. Figure used from Ref. [159] with permission from the American Chemical Society, Copyright 2015

cation also forms a three-fold inner-sphere coordination, but with less symmetric second-sphere structures [160].

As noted earlier, the interaction between vanadium ions and acetylene molecules is quite different from that of the other transition metals, prompting us to examine its behavior as multiple acetylenes are added around the metal. Figure 6.13 shows some of the spectra and structures obtained. The di-acetylene complex forms a bow-tie structure, with each of the two acetylenes bound in a three-membered ring metallacycle like that seen for the mono-acetylene complex. When three acetylenes are added, the spectrum becomes more complex, with several more vibrational bands spread over a wider frequency region. Additionally, the spectrum varies with the concentration of acetylene added to the experiment. The third trace down in the figure shows the spectrum measured at lower acetylene concentration (2.5% in argon), while the lower trace shows the spectrum measured with higher concentration (15%). The multiband spectrum at lower concentration can be assigned to two isomers, primarily the one shown with both three- and five-membered metallacycle rings, and a

**Fig. 6.13** The infrared spectra and structures formed from the addition of multiple acetylene ligands around vanadium ions. The third trace down shows the spectrum for  $V^+(C_2H_2)$  at low concentration, while the bottom trace shows the same mass ion when acetylene is added at higher concentration. Cyclization chemistry occurs, which eventually forms benzene

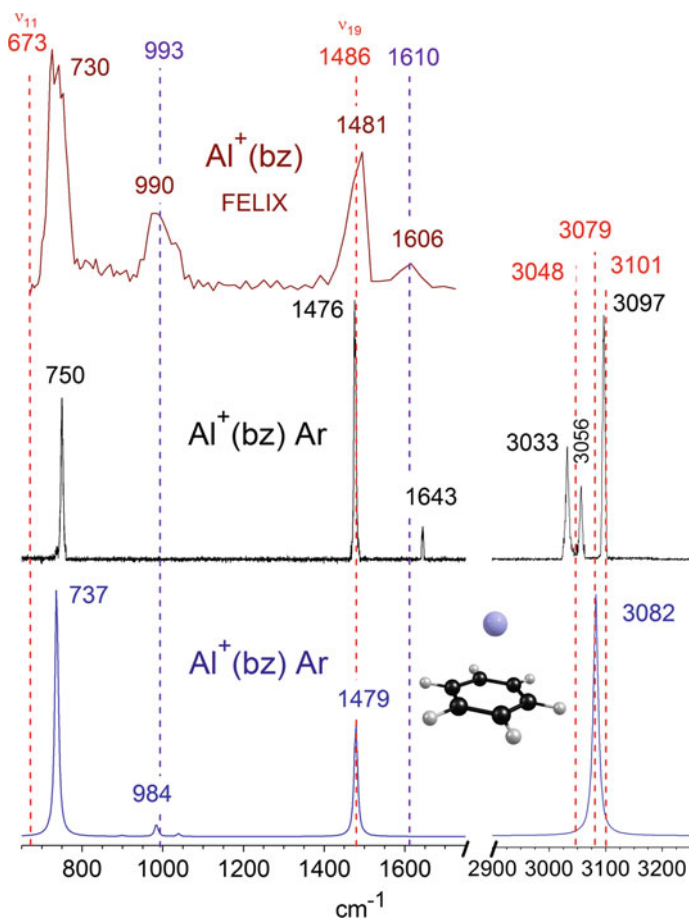


secondary one with three, three-membered metallacycle rings. The single band in the lower spectrum is assigned to the  $V^+(\text{benzene})$  complex! This is predicted by theory, which shows that this isomer is the most stable for this composition, and it can also be confirmed by producing the same mass ion directly from benzene and measuring its spectrum, which is identical to that shown here. The structures mentioned for the spectrum of  $V^+(\text{C}_2\text{H}_2)_3$  at low concentration have been implicated in previous theoretical work on other metal–acetylene systems as intermediates along the reaction path to form benzene via the cyclization of acetylene. Apparently, we have observed the same kind of cyclization chemistry here for the vanadium cation system too. Although the cyclization of acetylene to form benzene is a known chemistry on a number of different catalysts, the mechanism for the reaction has always been uncertain. Our infrared spectra at low concentration reveal for the first time the specific intermediate structures involved. Additional work will be necessary to understand the concentration dependence in more detail and to determine whether other metal ions might catalyze similar cyclization chemistry.

## 6.6 Metal–Benzene Complexes

Metal–benzene complexes are known for the formation of sandwiches, and cation– $\pi$  interactions are well studied in organometallic chemistry [6–11, 16, 279–282]. These systems have been studied in gas phase ion chemistry and in computational chemistry [289–306]. As shown in previous studies in our lab, the interaction of metal cations with the aromatic  $\pi$  system has distinctive effects on vibrational spectra. Charge transfer from the ring system toward the metal induces a red shift on the in-plane carbon ring distortion,  $\nu_{19}$  ( $1486\text{ cm}^{-1}$  in isolated benzene), while this also causes a blue shift in the out-of-plane hydrogen bend,  $\nu_{11}$  ( $673\text{ cm}^{-1}$  in isolated benzene) [167, 302]. We documented these patterns for several cation–benzene systems in work done at the FELIX free electron laser using infrared multiphoton photodissociation (IR-MPD) spectroscopy on the ions without tagging [201–203], as the cluster source available at that time did not allow sufficient cooling for the formation of rare gas adducts. Unfortunately, the conditions used for the IR-MPD process can cause significant power broadening in spectral lines and shifts to lower frequencies. Rare gas tagging has not yet been applied to transition metal–benzene complexes, except for spectra in the C–H stretching region [165, 166]. The vibrations most sensitive to the metal–benzene charge transfer are in the fingerprint region, and therefore the details of this chemistry are yet to be revealed.

The most well-studied metal ion–benzene complex is  $\text{Al}^+(\text{benzene})_n$ , for which we have measured spectra for the  $n = 1\text{--}4$  complexes using argon tagging [168]. The spectrum for the  $n = 1$  complex is shown in Fig. 6.14, where it is compared to the spectrum reported previously for this complex using IR-MPD with the FELIX free electron laser [202]. As shown, the quality of these tagged spectra is now far superior to the previous work in signal levels and resolution. Bands which were broad in the IR-MPD spectrum are much sharper, and the shifts from the IR-MPD process



**Fig. 6.14** The IR spectrum of  $\text{Al}^+(\text{bz})$  in the C–H and fingerprint regions, measured with argon tagging (middle) compared to that measured with IR multiphoton dissociation spectroscopy with the FELIX free electron laser (top). The lower trace (blue) shows the spectrum predicted by theory. The C–H stretch region has a triplet structure from a Fermi resonance, as seen in isolated benzene. Figure used from Ref. [168] with permission from the American Chemical Society, Copyright 2014

apparently occur in an unpredictable way at both higher and lower frequencies for different bands. The light red dashed lines in the figure show the positions of the free-benzene IR-active vibrations, including the well-known Fermi resonance that splits the single C–H stretch expected into a triplet [307]. The purple dashed lines show the positions of Raman-active (IR-inactive) vibrations, which appear in the IR spectrum of the metal ion complex because of its reduced symmetry. The red shift in the  $\nu_{19}$  band associated with charge transfer is only  $10\text{ cm}^{-1}$ , whereas the blue shift of the  $\nu_{11}$  out-of-plane bending mode is  $75\text{ cm}^{-1}$ . The former is much smaller than the shifts seen for transition metal complexes, consistent with their expected greater charge transfer, but the latter is comparable to the shifts seen before because it arises from

the mechanical action of the bending hydrogen molecules bumping into the metal. The data on the larger complexes reveals that the coordination around  $\text{Al}^+$  contains *three* benzene molecules, that is, it does not form the same kind of sandwich seen for transition metals. Clearly, the quality of spectra for tagged ions is highly desirable, and our lab is working to get similar data for transition metal ion complexes. Ongoing work has obtained partial spectra for  $\text{V}^+(\text{bz})$  and for  $\text{Co}^+(\text{bz})_2$  [308]. Both of these systems exhibit multiplet structure in the  $\nu_{19}$  vibration, indicating that the benzene ring is distorted from its  $\text{D}_{6h}$  symmetric structure by the strong metal binding.

Although metal ion–benzene systems have been studied for many years, their electronic structure remains a significant challenge. In the case of  $\text{V}^+(\text{benzene})$  and  $\text{V}^+(\text{benzene})_2$ , ordinary DFT (B3LYP or BP86 functionals with large basis sets) misses the ground state spin configuration (triplet predicted; quintet agrees with experiment and higher level theory) [165, 201]. Higher levels of theory get the correct quintet spin state for this system [304, 305]. For  $\text{Ni}^+(\text{benzene})_2$ , DFT apparently gets the wrong ground state structure ( $\eta^4$  sandwich predicted;  $\eta^6$  observed) [166]. As in the case of other systems, the 18-electron rule is a useful guiding principle for metal ion–benzene complexes.  $\text{Mn}^+(\text{benzene})_2$  is isoelectronic to the known neutral dibenzene chromium species, but the infrared spectrum of this ion has not yet been measured in the gas phase. Its expected  $\eta^6$  coordination on the six-fold axis of benzene is common for many metal ions. However, later transition metal ions have more valence electrons, and do not need to interact with all six  $\pi$  electrons to achieve the 18-electron configuration. Some of these systems are known to adopt  $\eta^4$  or lower coordination in the condensed phase, and then their sandwich structures should have the two rings offset from each other. In extreme cases, some transition metals are predicted to bind strongly enough to distort the planarity of the ring (e.g.,  $\text{Fe}^+$ ,  $\text{V}^+$ ,  $\text{Co}^+$ ,  $\text{Ni}^+$ ). All of these structures will lead to recognizable patterns in the fingerprint region. Future studies of these systems with tagging are therefore highly desirable.

A final aspect of these metal–benzene complexes worth mentioning is that the early transition metal systems, particularly vanadium, form multiple decker sandwich structures with unusual electronic structure and bonding [296–298]. IR spectra have been obtained for neutrals following cation deposition on surfaces, but not for ions. These systems will be even more challenging for future experiments and theory.

## 6.7 Conclusions

The studies described in this chapter illustrate how infrared photodissociation spectroscopy can be applied to a variety of metal–molecular complexes in the gas phase. These gas phase studies eliminate the effects of solvent or counterions and make it possible to investigate isolated molecules with different numbers of ligand or solvent molecules. Vibrational band patterns, in coordination with computational predictions, make it possible to determine the structures of these complexes, and the effects that metal binding has on the geometry and charge distribution of the molecular adducts. Additionally, the spectral patterns reveal the number of ligand or

solvent molecules making up the first (and sometimes higher) coordination sphere(s). In the case of carbonyl ligands, this provides an opportunity to make comparisons to several well-known neutral complexes that are isoelectronic analogs to the cations studied here. Because vibrational band patterns vary with the electronic state and spin multiplicity of the system, these spectra also make it possible to investigate the electronic structure of these complexes, and to identify strengths and weaknesses of density functional theory computations. We find examples in which DFT fails to describe the system adequately, such as the transition metal–benzene spin states, but also find many examples where it performs quite well to describe vibrational band patterns. The computations presented here usually use the B3LYP functional. We have tried other functionals, especially including dispersion-corrected versions which are believed to describe the energetics of bonding more accurately. However, our experiments do not probe bonding energetics; they measure IR spectra. For this application, we find that harmonic DFT/B3LYP calculations with proper scaling to account for anharmonicity provide the best description of vibrational patterns.

Although we have presented a variety of metal–molecular complexes here, there are clearly many more which could be investigated. Complexes with larger ligand or solvent molecules become more chemically interesting, and these studies can also be extended to metals other than the main group and transition metal species described here (e.g., lanthanides, actinides). We anticipate that this general area of activity will continue to provide fundamental insights into metal–molecular interactions for the foreseeable future.

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