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Infrared spectroscopy to probe structure and dynamics in metal ion-molecule complexes

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Infrared spectroscopy to probe structure and dynamics in metal ion–molecule complexes

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Vibrational spectroscopy measurements are described for mass-selected metal cation–molecular complexes using the technique of infrared resonance-enhanced photodissociation (REPD) spectroscopy. We discuss the mechanism of the REPD process in the infrared and how multiphoton techniques or rare gas tagging can be employed to facilitate dissociation processes in strongly bound complexes. Spectra are reported for $\text{Fe}^+(\text{CO}_2)_n$ complexes that demonstrate the formation of coordination spheres around the metal cation and for $\text{Mg}^+(\text{CO}_2)_n$ complexes, where the interaction with theory makes it possible to obtain structures for small clusters. Both of these studies investigate the asymmetric stretch region of CO_2 . $\text{Ni}^+(\text{C}_2\text{H}_2)_n$ complexes are studied in the C–H stretch region, demonstrating evidence for intracuster cyclization reactions. Finally, experiments are described for metal ion–benzene ($\text{M} = \text{V}, \text{Al}$) complexes excited in the benzene ring distortions and C–H bending region. These experiments confirm the π -bonded configuration of these complexes.

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1. Introduction

Metal ions and their complexes are ubiquitous in chemistry, biology, geochemistry and astrophysics. Inorganic chemistry employs solvated metals or coordination complexes as reagents or as homogeneous catalysts. Enzymes often have metal ions

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at their active sites and the binding here influences their structure and function [1, 2]. Subtle electrostatic forces govern the selective metal ion transport through cell membranes [3], the dynamics of host–guest chemistry [4] and the binding at catalytic metal oxide surfaces [5–7]. Toxic metals in soils and in stream water pose persistent environmental problems, and complexes of metal ions with aqueous species such as humic acids play a key role in this aquatic chemistry [8]. Metal ions (Na^+ , Mg^+ , Ca^+ , Si^+) are deposited in the Earth's outer atmosphere by meteor ablation [9–13]. Eventually, these metals are incorporated into aerosol particles that settle into the lower atmosphere [14]. Metal ions also occur in other planetary atmospheres [15], and their complexes (e.g. with polycyclic aromatic hydrocarbons) may be components of interstellar dust and ice grains [16–23]. In all these environments, metal ion–molecular interactions determine the outcome of significant chemistry. However, theory is often unable to describe these processes, particularly when multiple molecules condense around a single ion. It is therefore important to measure directly the details of metal ion–molecular bonding. Our laboratory does this via the study of $\text{M}^+ - \text{L}_x$ complexes that are produced in the gas phase and investigated with size-specific spectroscopy. Experiments on model complexes, in coordination with theory, can refine the understanding of bonding at metal centres, and this insight can be applied to more complex systems that occur throughout chemistry. In the present review, we describe our recent efforts employing infrared (IR) laser spectroscopy as a probe of structure and dynamics in these metal ion complexes.

Metal ion complexes have been a focus area of gas phase ion chemistry for many years, and there are numerous studies of the reactions and energetics of these systems [24–26]. Equilibrium mass spectrometry measurements [27–29], radiative association measurements [30] and threshold collision induced dissociation experiments [31–33] have determined metal ion–ligand binding energies, and from these measurements coordination numbers have been inferred. Theory has investigated the structures of metal ion complexes and their bonding energetics [34–54]. Transition metal ions are often reactive with ligands, and the insertion and elimination chemistry in these systems has been investigated [24, 25]. Metal ions have been produced selectively in specific electronic states to study the effects of electronic configuration on reactivity [26]. More recently, metal ion chemistry has been fascinated with the effects of solvation or multiple ligand interactions. Intermolecular reactions have been documented to begin only after the metal ion is bound to multiple ligands [55], and likewise size-specific intramolecular reactions between the metal and ligand/solvent molecules or between ligand/solvent molecules have been suggested from mass spectrometry patterns [56–59]. Theory has investigated these effects [45, 60], but there is little in the way of spectroscopic characterization of these systems that might reveal the exact chemical species present.

The development of the laser vaporization source [61] for the production of gas phase metal atoms, ions and clusters contributed in a positive way to studies of metal ion chemistry, making it possible to obtain ions of virtually any metal in high density. Likewise, when laser sources became available, studies of metal ion spectroscopy began to progress because of the high densities possible [62]. Studies of neutral metal diatomics and triatomics were conducted using resonant laser ionization spectroscopy [63], and studies of larger metal clusters were accomplished via laser photoelectron spectroscopy of size-selected anions [64–66]. As part of this focus on metal systems, metal ion complexes began to be studied with mass-selected laser photodissociation spectroscopy [67–88]. This method was preferred because the

low densities of metal ion complexes preclude their study by absorption techniques, and because of the strong tendency of these systems to form a distribution of cluster or complex sizes. Various mass spectrometer configurations were employed to mass select metal-containing ions from the distributions formed, to photodissociate them and to measure the dissociation yield as a function of energy. Because of the pulsed laser sources employed and the required high intensity lasers, these experiments have been most often carried out using pulsed dye lasers or, more recently, pulsed optical parametric oscillator (OPO) systems. Likewise, because of sensitivity and energetic considerations, these experiments began in the ultraviolet (UV)–visible region of the spectrum, focusing on electronic spectroscopy.

Electronic spectroscopy has been applied to both main group [67–86] and transition metal [87, 88] ion complexes with rare gas atoms or with small molecules. In both systems, the strategy has been to choose metal ions with known atomic resonances at low energy. If weakly bound electrostatic complexes form, then the electronic spectra of these complexes are expected to occur near the atomic transition. This strategy is particularly effective for the group II metal ions (Mg^+ , Ca^+ , Sr^+ , Ba^+) which have intense atomic resonances corresponding to the ($^2\text{P} \leftarrow ^2\text{S}$) atomic transitions [67–85]. Electronic spectra of magnesium and calcium ion complexes with the rare gases and molecules such as H_2O , CO_2 , N_2 , C_2H_2 , C_2H_4 and CH_3OH have been studied by our group [67–80], by Fuke and co-workers [82] and by Kleiber and co-workers [83] using photodissociation spectroscopy. Similar photodissociation measurements have been described by Farrar and co-workers [81] and Velegrakis and co-workers [84] for strontium ion complexes. Although aluminium cations have no low energy atomic resonances, vacuum UV techniques have been employed to obtain electronic spectra for $\text{Al}^+ - \text{Ar}$ [86] and $\text{Al}^+(\text{C}_2\text{H}_4)$ [83(b)]. Brucat and co-workers [87], and more recently Metz and co-workers [88], have used electronic photodissociation studies to investigate transition metal cation complexes with some of the same small molecules indicated above. Similar methods have been used by several groups to study electronic spectra of multiply charged transition metal cation complexes [89, 90]. As a complement to these electronic spectroscopy measurements, various theoretical calculations have also been performed on ground and excited states of metal ion complexes [34–54]. These have produced structures for monoligand species and in some cases for multiple-ligand complexes.

Unfortunately, the progress in understanding cluster structures and growth dynamics has been rather limited because electronic spectroscopy becomes problematic in multiple-ligand clusters [80]. Monoligand species often provide vibrationally resolved spectra, and extrapolations of progressions in the metal–ligand stretching coordinate lead to estimates for dissociation energies. In some cases, rotationally resolved spectra have been obtained, leading to determination of structures for monoligand complexes [68, 72, 73, 76–78]. However, it has been difficult to obtain such detailed information from the spectra of multiligand systems. Predissociation is often enhanced in these species, leading to severe broadening in spectra, and vibrationally resolved spectra are rare [80]. Another complication is photoinduced reactions. Although many metal ions form weakly bound electrostatic complexes in their ground states, electronic excitation is often enough to overcome reaction barriers and metal–ligand reactions may occur. This may cause lifetime broadening in spectra, again resulting in the loss of vibrational structure. Finally, ground state reactions may also occur, induced spontaneously by the effects of multiple ligand solvation. This effect has been documented via mass spectrometry patterns, for

example, for a number of metal ion–water cluster systems. Fragmentation of $M^+(H_2O)_n$ clusters produces metal hydroxides, suggesting that solvation has taken place to generate M^{2+}, OH^- within the cluster [56–60]. This presumed ion pair may be in ‘contact’ or it may be ‘solvent separated’ in larger clusters. Again, such chemistry is quite fascinating, but electronic spectra of these systems are broad and structureless.

It is therefore apparent that electronic spectroscopy has limitations for cluster studies of this sort and that other techniques that probe the ground electronic state might be more effective. In the ground state, predissociation and photoinduced reactions are unlikely, and even if solvation-induced processes occur they might be evident in the vibrational spectrum. Two general approaches have been tried to probe the ground state. Zero electron kinetic energy photoelectron spectroscopy employs one- or two-photon photoionization of neutral precursor complexes, and ionization occurs near the threshold energy [91–95]. The vibronic structure measured in this method probes the corresponding ground state. Since there is a significant change in the bonding between neutral and cation metal systems, the Franck–Condon activity measured in these spectra is usually in the metal–ligand stretch coordinate. Size selection is not generally possible for neutrals, but size-dependent ionization thresholds can be used for some size selection in these experiments. IR spectroscopy is of course the standard method to probe ground state vibrational structure, but this method is difficult for low density ion beams produced by a pulsed source. Direct absorption techniques are therefore not possible. In the same way that mass-selected photodissociation became attractive for electronic spectroscopy because of sensitivity and size selection issues, IR photodissociation can provide vibrational spectroscopy for ground state metal ion complexes. There have been many studies of IR photodissociation spectroscopy of non-metal cations and anions and their clusters [96–103]. Likewise, neutral clusters have also been studied by IR photodissociation [104–106]. Lisy and co-workers were the first to exploit these same methods for the study of metal complexes in their work on alkali cation systems [107]. Our work, as described in this review, combines this same methodology with pulsed metal ion production from the laser vaporization cluster source [108–113]. This makes it possible to produce metal cation complexes with a variety of higher melting metals including both main group and transition metal systems. In this work, we show how IR spectroscopy can be used to determine the structures of multiligand complexes, to document the number of molecules in the coordination sphere around the metal and to discover novel ligand–ligand intracluster reactions.

2. Experimental methods

Metal complexes are produced in our laboratory by laser ablation [61, 67] of rotating-rod targets in a pulsed-nozzle source, using a supersonic expansion seeded with the molecular vapour of interest. Complexes grow directly as cations, or they can be produced by ultraviolet laser (ArF; 193 nm) photoionization of neutrals. The third harmonic of a Spectra Physics Nd:YAG laser (Quanta Ray INDI 10) is used to vaporize a rotating metal rod target with a typical energy of 1–2 mJ/pulse. Clusters are formed in a supersonic expansion using a General Valve (series 9) with a backing pressure of 40–60 psi. Metal ion–molecular complexes are formed by adding a partial pressure of the molecular vapour of interest to the rare gas (helium or argon) expansion mixture. The molecular beam machine for these studies consists of a

cluster source chamber and a differentially pumped mass spectrometer chamber, as shown in figure 1. The expansion produced is skimmed into the detection chamber and cation clusters are extracted from the molecular beam with pulsed acceleration plates into a reflectron time-of-flight (RTOF) mass spectrometer. They are mass selected by their time of flight using a pulsed deflection plate assembly known as the 'mass gate', located prior to the reflectron field region. The details of mass selection and photodissociation in the RTOF instrument have been described previously [67, 114].

An IR optical parametric oscillator/amplifier (OPO/OPA) laser (Laser Vision) pumped by a Continuum 9010 injection-seeded Nd:YAG laser is used to photodissociate the clusters [108, 109]. This system has two 532 nm pumped KTP crystals

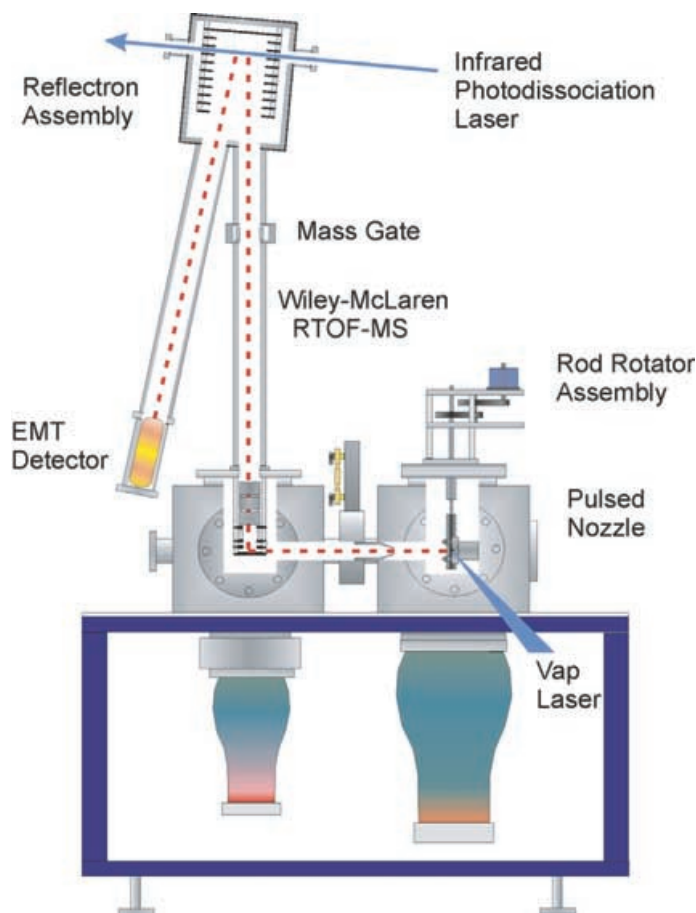


Figure 1. Schematic diagram of the molecular beam machine used for mass-selected photodissociation spectroscopy of metal ion complexes. The complexes are produced by laser vaporization in a pulsed-nozzle cluster source in the main chamber (right), and they are detected with an RTOF mass spectrometer in a differentially pumped second chamber (left). Pulsed deflection plates in the flight tube can be activated for mass selection, and laser excitation takes place in the turning region of the reflectron field. The appearance of fragment ions as a function of the wavelength provides the photodissociation spectrum.

in the grating tuned oscillator section and four KTA crystals in the amplifier section. The signal output from the oscillator is combined with the residual 1064 nm in the amplifier, and difference frequency generation here provides the tunable near-IR output from 2.2 to 4.9 μm (4500–2050 cm^{-1}). Pulse energies ranging from 15 to 1 mJ respectively and the linewidth is on the order of 0.3 cm^{-1} . In so-called ‘low power’ experiments, the unfocused laser is used, which has a pulse energy of 1–3 mJ/pulse near 2350 cm^{-1} and 7–10 mJ/pulse near 3000–3400 cm^{-1} . In so-called ‘high’ laser power conditions, this light is focused with a 25 cm focal length lens.

The mass-selected clusters are excited with the IR light in the turning region of the reflectron. The laser beam is focused or not, depending on the fragmentation efficiency required for different clusters. Residual parent ions and any fragments are mass analysed by their time of flight through a second drift tube section. IR photodissociation spectra are recorded by monitoring the fragment intensity in one or more channels as a function of the IR wavelength. A typical spectrum is obtained with a 0.5 cm^{-1} scan step and averaged over 250 laser shots. The ion signals are recorded with a digital oscilloscope (LeCroy WaveRunner 341) connected to a PC via an IEEE-488 interface.

Figure 2 shows a mass distribution of $\text{Fe}^+(\text{H}_2\text{O})_n$ clusters produced in our instrument. As shown, complexes containing up to 30 or more solvent molecules are produced. Any one of these may be size selected for photodissociation studies. Figure 3 shows an example of a photodissociation mass spectrum of mass-selected $\text{Al}^+(\text{C}_2\text{H}_2)_8$ when it is excited with the IR laser near the C–H stretching region. As

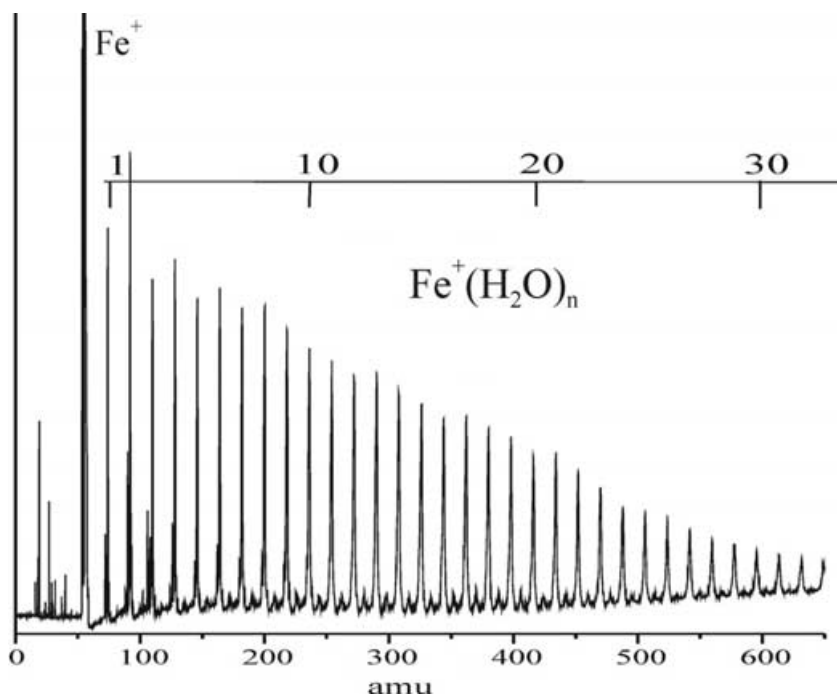


Figure 2. A typical mass distribution of $\text{Fe}^+(\text{H}_2\text{O})_n$ complexes produced by the cluster source. For measuring the full mass spectrum like this, the pulsed deflection plates for mass selection are turned off. As shown, complexes are formed containing up to 30 or more water molecules attached to the iron cation.

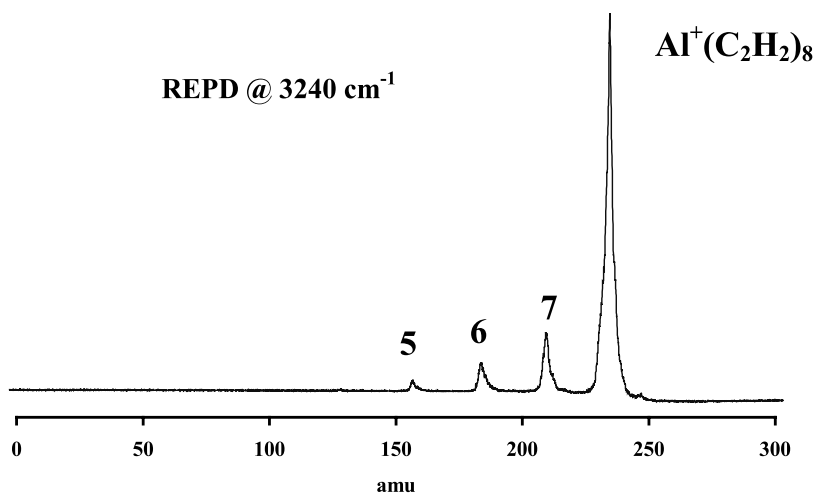


Figure 3. An example of a photodissociation mass spectrum. For this measurement, the $\text{Al}^+(\text{C}_2\text{H}_2)_8$ cation complex is mass selected with the pulsed deflection plates and excited with the IR laser tuned to a resonance in the C–H stretch region. The fragment ion peaks labelled 5, 6 and 7 are only formed when the IR laser is present, tuned into a resonance and timed to intersect the parent ion in the turning region of the reflectron. This shows that resonance-enhanced photodissociation (REPD) occurs, resulting in the sequential elimination of one, two or three acetylene molecules.

shown, the photofragments indicate the elimination of one to three acetylene molecules from the cluster. IR photodissociation spectra are recorded by monitoring the intensity of one or more of these fragment ion channels as the IR excitation laser is scanned.

Additional experiments in the area of infrared photodissociation are done by our group in collaboration with the group of Meijer and co-workers in the Netherlands [112, 113]. These experiments employ a similar cluster source, but ions for photodissociation are produced primarily by ArF (193 nm) photoionization of neutrals in the center of a quadrupole ion trap. Ions held in this trap are excited with a tunable infrared free electron laser known as ‘FELIX’ (free electron laser for IR experiments) [115]. This laser provides high intensity (up to 50 mJ/pulse) of IR in the region 400–1700 cm^{-1} . It has a higher pulse energy and different temporal pulse structure to the OPO systems that we use and it covers the lower frequency region that is not accessible with the OPO. Except for the different mass spectrometer and excitation laser, IR photodissociation experiments with FELIX employ essentially the same methodology as those using the OPO system.

3. The infrared photodissociation mechanism

A key issue in IR photodissociation experiments is the photon energy compared with the energy needed to break a bond. In electronic photodissociation experiments, visible and UV lasers are used that have photon energies in the range from 12 000 to 50 000 cm^{-1} . However, the range of molecular vibrational fundamentals [116], which occurs only up to about 4000 cm^{-1} , dictates that low energy photons must be used for IR photodissociation if the excitation is to be employed on resonance. Main group metal ion–molecular complexes may have purely electrostatic bonding, in

which case the most strongly bound species would be ion–water [31, 33, 34, 37, 45–47, 57, 68, 73] or ion–benzene [31, 50–54] complexes (dissociation energies near 1 eV, or about 8000 cm^{-1}). Electrostatic metal ion– CO_2 complexes have bond energies near 5000 cm^{-1} [31, 35, 40, 69], while similar metal ion–acetylene or ethylene complexes have bond energies near 6000 cm^{-1} [31, 38, 77]. Clearly, one-photon IR excitation on the fundamentals of ligand vibrations would not be energetic enough to cause fragmentation in these systems. The situation is worse for transition metal ion complexes, where partial covalent interactions result in even higher binding energies. For example, transition metal ion–benzene complexes may be bound by 2–3 eV [50–54]. On the other hand, as cluster size increases, it is often true that the binding energy of the outermost ligand becomes weaker. This is especially true after the first coordination layer is completed, when subsequent ligands bind on top of other ligands and are not attached directly to the metal ion. In this scenario, the binding energies should be more like those of the isolated molecular dimer or trimer, which are expected to be much lower. In general, we expect that IR photodissociation will be difficult for small complexes ($n = 1\text{--}3$) with higher binding energies and that this process will become more efficient as cluster size grows. This is consistent with our observations, as described below. Eventually, as cluster size becomes extremely large, the *rate* of dissociation may become so low that it cannot be measured, depending on the specific instrumental configuration employed.

Two general approaches can be used to achieve IR photodissociation in the more strongly bound systems. Multiphoton dissociation (MPD) was described many years ago for metal-containing ions in ion cyclotron resonance (ICR) mass spectrometers excited with CO_2 lasers [117]. Likewise, the general mechanism of multiphoton dissociation applicable for neutrals or ions has been extensively investigated [118–122]. With the efficiency of new OPO lasers and especially with the high pulse energy available from free electron lasers, similar multiphoton processes are indeed possible in our experiments. The efficiency of MPD depends on the laser pulse energy and its temporal structure, the binding energy of the complex and the density of its vibrational states as a function of energy. Vibrational state density above the fundamental level facilitates multiphoton absorption by maintaining the resonance that would otherwise be lost by anharmonicity effects. The density of states is also critical for intramolecular vibrational redistribution (IVR) of energy from the ligand vibration excited to the dissociation coordinate (usually the metal–ligand stretch). Since the density of states increases with the size of the complex, MPD is expected to be more efficient for larger complexes. As shown below, IR multiphoton processes are possible with nanosecond pulsed OPO lasers, but their efficiency is limited. On the other hand, the efficiency of 10–20 photon dissociation (or even higher-order processes) can be extremely high with the high pulse energy and micropulse train temporal profile of a free electron laser.

Another approach used often in photodissociation spectroscopy has been the addition of a weakly bound spectator atom or molecule, usually a rare gas atom, to the cluster [96, 98, 123, 124]. If such a weakly bound tag is employed, then the perturbation of the cluster structure and its vibrational spectrum is expected to be minor, and the dissociation yield is enhanced. IVR transfers energy throughout the cluster, and the binding energy of the tag is weakest, so that this species is eliminated more easily than other ligands. The binding energies of rare gas atoms are usually weak enough so that single-photon excitation, even in the IR, is enough to cause dissociation. The addition of a weakly bound tag atom or molecule to the cluster

also adds low frequency vibrations which in turn increase the density of states and promote IVR and dissociation rates. In the work described here, both multiphoton processes and rare gas tagging are employed to achieve efficient IR photodissociation of metal ion complexes.

4. Infrared resonance-enhanced photodissociation spectroscopy

As we and others have shown, the efficiency of single-photon or dissociation and MPD processes is strongly enhanced when the first photon is tuned onto resonance with a vibrational transition. This makes it possible to obtain vibrational spectroscopy with the photodissociation method. The resonances measured this way are expected to occur at the same positions as those in the conventional IR absorption spectrum. However, the line intensities measured in this way will be modulated by the dissociation efficiency, and this may cause variations from those in the absorption spectrum. Different terms have been employed for spectroscopy measured in this way including IR resonance-enhanced MPD or just IR-REPD. While some of our processes are undoubtedly multiphoton in nature, others are definitely not. We therefore prefer to use the more general REPD term to describe our measurements.

4.1. $Fe^+(CO_2)_n$ complexes [108]

Metal ion– CO_2 complexes were selected as initial candidates for our IR photodissociation experiments because of the strong IR absorption expected for the ν_3 asymmetric stretch vibration of CO_2 which occurs within the tuning range of our OPO laser system. The vibrational frequencies of an isolated CO_2 molecule are well known (ν_1 , ν_2 , ν_3 (symmetric stretch, bend, asymmetric stretch) = 1333, 667 and 2349 cm^{-1}) [116]. Many metal ion– CO_2 complexes have been studied by previous experiments [31, 69, 75, 87] and theory [35, 40], and the binding energies for the small complexes are known. Likewise, much is known about clusters of CO_2 molecules without metal [125–129], so that comparisons of IR spectra can be made. $Fe^+(CO_2)_n$ complexes provide a good test for the IR-REPD method because they are strongly bound but also have strong IR absorption. The dissociation energy of the $n = 1$ complex has been measured with collision-induced dissociation and equilibrium mass spectrometry measurements [130, 131] to be about 5000 cm^{-1} .

$Fe^+(CO_2)_n$ complexes out to $n = 20$ or so are produced with high efficiency by our cluster source. Size selection followed by IR excitation near 2349 cm^{-1} produces relatively efficient photodissociation for clusters in the $n \geq 3$ size range. However, the $n = 2$ cluster could only be dissociated with full laser power and focusing with a 25 cm lens. The $n = 1$ complex could not be photodissociated under any laser power conditions. This behaviour is consistent with the strong bonding and low density of vibrational states expected for the small clusters, as discussed above. The clusters that dissociate do so by eliminating whole CO_2 molecules. At larger cluster sizes, multiple molecules are eliminated, and the number varies with the laser power. In principle, the laser power dependence of these signals could be used to determine how many photons are required for photodissociation. However, the laser vaporization cluster source suffers from poor shot-to-shot stability, making systematic studies of this sort quite difficult. In some cases, no dissociation is observed with the full power of the unfocused laser and signal is found only when the laser is focused. However, focusing changes the overlap between the laser and the ion beam in a way

that is difficult to quantify. For these reasons, we do not report the results of specific laser power studies.

The photodissociation yield is indeed wavelength dependent, as expected for an REPD process. Figure 4 shows selected spectra for $\text{Fe}^+(\text{CO}_2)_n$ complexes ($n = 2, 3, 5, 6$) measured in the $n = 1$ fragment ion channel [108]. To our knowledge, these data represent the first time that IR spectroscopy has been carried out for transition metal ion–molecule complexes. As shown in the figure, these spectra are rather broad, with linewidths no better than about 30 cm^{-1} full width at half-maximum and the $n = 2$ complex has structure covering almost 100 cm^{-1} . Such broad linewidths are again consistent with expectations for multiphoton processes, where the resonance enhancement can be obtained near resonance and the high laser pulse energy employed leads to some power broadening. In addition, while the dissociation yield may be low for cold complexes, it will be higher for vibrationally unrelaxed complexes that already contain some internal energy. These hot molecules may represent a minor concentration in the molecular beam, but their higher dissociation efficiency can cause them to contribute more to the spectral linewidth, and they may absorb either to the red or the blue of cold species depending on the details of anharmonicity and vibrational mode couplings. Nevertheless, in all of these spectra, it can be seen that the main peaks are found to the blue of the resonance in the free CO_2 molecule. Such a blue shift in these resonances is understandable, if we consider the likely structural arrangement of CO_2 in contact with a metal cation. In previous spectroscopy studies of metal ion complexes with one CO_2 molecule, the structure

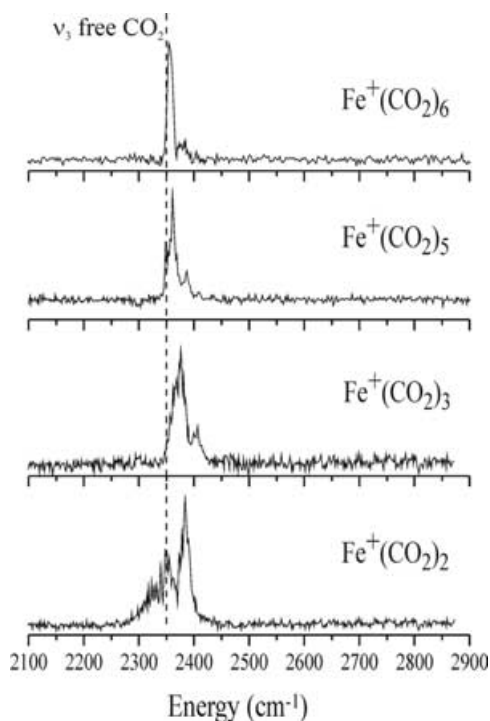


Figure 4. The IR-REPD spectra of small $\text{Fe}^+(\text{CO}_2)_n$ complexes measured in the $n = 1$ fragment ion channel. The broken line shows the position of the asymmetric stretch (ν_3) resonance for an isolated gas phase CO_2 molecule.

has been determined in every case to be linear (i.e. $M^+ \cdots O=C=O$) as a result of the charge–quadrupole electrostatic interaction [69, 75, 87]. This structure was also found in electronic spectroscopy of $Fe^+(CO_2)$ [132], and this structure has been predicted by theory for this complex [40,133]. A shift to higher frequency for the asymmetric stretch results because of the increased repulsion at the inner turning point of this vibration due to the presence of the metal ion in this linear configuration.

Although these new IR data are encouraging, the quality of the spectra is not as great as we would like. To improve the signal and to reduce the linewidths obtained, we use the rare gas tagging method employed previously by other groups [96, 98, 123, 124] and discussed above. The belief is that an attached rare gas does not introduce a significant perturbation to the spectroscopy, but it provides a weaker bond and a greater density of vibrational states to improve the photodissociation efficiency. Figure 5 shows the effect of argon tagging on the $Fe^+(CO_2)_2$ spectrum. It is clear that much of the broad structure is removed and a simple one-peak spectrum is obtained when one argon is attached to the complex. The signals are weaker, but attaching a second argon produces a spectrum in essentially the same position. This supports the notion that the argon is indeed a ‘spectator’ that promotes the spectroscopy without perturbing it.

Similar improvements are obtained for all the small $Fe^+(CO_2)_n$ complexes seen here, as shown in figure 6. In every case but the $n = 1$ species, tagging with a single

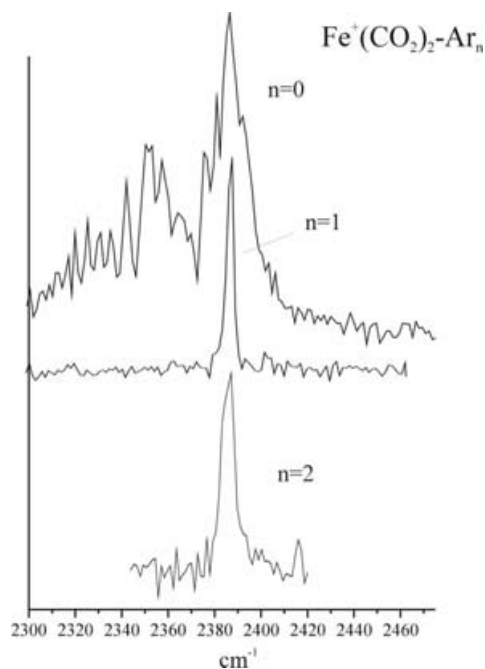


Figure 5. The effect of ‘argon tagging’ on the IR-REPD spectrum of $Fe^+(CO_2)_2$. The upper trace shows the spectrum measured when the parent ion is selected and excited, and the spectrum is measured in the $Fe^+(CO_2)_1$ fragment channel. The middle and lower traces show the spectra for $Fe^+(CO_2)_2-Ar_1$ and $Fe^+(CO_2)_2-Ar_2$ measured by the loss of argon.

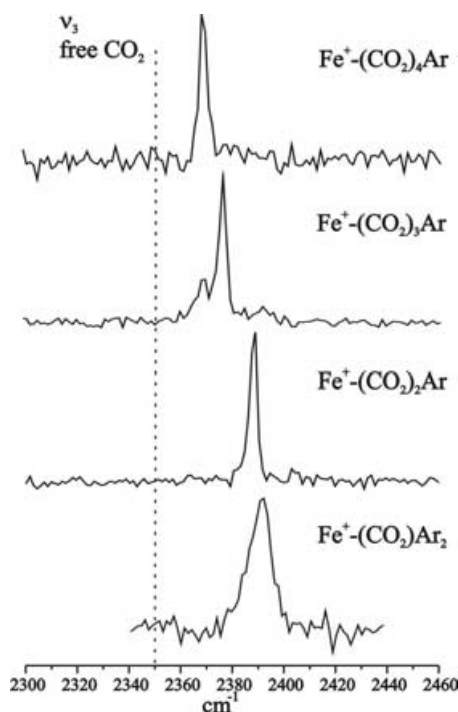


Figure 6. The spectra of small $\text{Fe}^+(\text{CO}_2)_n$ complexes measured by argon tagging. In all except the $n = 1$ complex, tagging occurs with a single argon atom. The $n = 1$ complex requires at least two argon atoms before IR-REPD can be observed.

argon atom is enough to produce a sharp spectrum with a high dissociation yield. It is clear from these data that each complex has a spectrum consisting of one primary band, and this band is blue shifted from the position of the free CO_2 asymmetric stretch. The blue shift is the greatest for the $n = 1$ and 2 complexes and decreases gradually for the $n = 3, 4$ species. We cannot produce argon-tagged masses for the $n = 5$ and larger species with enough intensity for these studies, suggesting that there is a significant change in the way that argon binds after $n = 4$. This is the first piece of information suggesting that five ligands (five CO_2 or four CO_2 and one argon) complete the first coordination sphere around the Fe^+ cation.

The simple IR spectra with one peak each for these clusters provide insight into the structures of these complexes. As noted above, the blue-shifted spectrum for the asymmetric stretch in the $n = 1$ complex is completely consistent with previous experiments and theory that suggested a linear structure for this ion [40(b), 132, 133]. The one IR band seen for $\text{Fe}^+(\text{CO}_2)_2$ indicates that this ion has an all-linear structure ($\text{O}=\text{C}=\text{O}\cdots\text{Fe}^+\cdots\text{O}=\text{C}=\text{O}$). The possible vibrational modes for this complex in the region of the asymmetric stretch include in-phase and out-of-phase stretches on the two ligands. In the same way that the symmetric stretch (ν_1) of a single CO_2 molecule is IR forbidden, the in-phase asymmetric stretch of the $n = 2$ complex is also forbidden if the complex is all linear, while the out-of-phase mode is IR allowed. If the complex were bent, both of these modes would be IR active in the same way that the symmetric and asymmetric stretch are both active for the H_2O molecule. Consistent with this, theory predicts this all-linear structure for the $n = 2$

complex [133]. Similar arguments based on the IR activity of in-phase and out-of-phase ligand vibrations for the $n = 3$ and 4 complexes suggest that these species must also have highly symmetric structures (trigonal planar for $n = 3$ and tetrahedral or square planar for $n = 4$ [108]).

The argon tagging results above suggested a change in ligand binding that occurs in these complexes near $n = 4$ or 5, consistent with the completion of a coordination sphere at this size. Additional information in this regard is provided by expanded views of the spectra for complexes in this size range that were studied without argon tagging, as shown in figure 7. In the lower trace, the spectrum of the $n = 4$ complex is shown. It has a broad blue-shifted band, which sharpens with argon tagging. However, in addition to this main feature, there is a weak shoulder band on the lower energy side that falls just at the frequency for the free CO_2 asymmetric stretch. The interpretation of this weaker band is possible by consideration of the many previous studies of the IR spectroscopy of pure CO_2 clusters [125–129]. As shown in these studies, when CO_2 clusters with itself, the asymmetric stretch vibration is only very weakly shifted (by $1\text{--}2\text{ cm}^{-1}$) from its free molecule value. We therefore expect to find a similar vibrational band in these metal-seeded clusters at or near the free CO_2 frequency whenever we have CO_2 molecules not coordinated to metal but instead clustering on other CO_2 molecules, i.e. in the second layer. In the $n = 4$ spectrum, there is just a weak feature here, and it goes away when we argon tag this

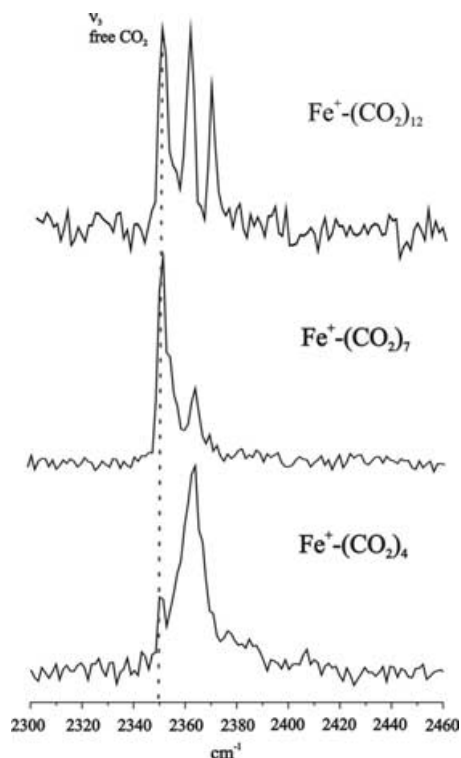


Figure 7. The IR-REPD spectra of $\text{Fe}^+(\text{CO}_2)_n$ complexes for $n = 4, 7$ and 12 measured without argon tagging. The additional bands for larger complexes are attributed to the molecules in outer layers not attached directly to metal.

cluster. This suggests that the feature is caused by the presence of a minor concentration of an isomer with at least one external CO₂ (i.e. a 3 + 1 structure). In the middle trace of figure 7, we see the spectrum for the $n = 7$ complex. It has the blue-shifted band, corresponding to CO₂ molecules coordinated to the metal, which we now designate as the 'core' feature. In addition, there is now a much stronger band at the free molecule frequency, corresponding to CO₂ molecules not coordinated to the metal. The intensity of this peak rises gradually between $n = 4$ and 7, and the intensity at $n = 7$ suggests that all complexes in the cluster distribution at this mass have external CO₂ molecules. We refer to this band as the 'surface' CO₂ band in these complexes. These results and the difficulty in argon tagging the clusters after $n = 4$ suggest that the coordination sphere for CO₂ around Fe⁺ is about five molecules. However, the cut-off in behaviour is gradual and not sharp. A much sharper cut-off has been seen recently in our laboratory for Ni⁺(CO₂)_{*n*} complexes, where the inner coordination number is exactly 4 [134]. A final vibrational feature apparent in these spectra begins to appear at $n = 9$ and is clearly evident in the spectrum for $n = 12$ shown in the upper trace of figure 7. An intermediate band occurs with a blue shift between the core and surface bands. A vibrational band at about this frequency has been measured previous for large CO₂ clusters which have 'interior' CO₂ confined by outer layers of CO₂ [125(a)]. This caging effect hinders the asymmetric stretch vibration and drives it toward higher frequency in much the same way that binding to metal does, but the interaction is weaker. We therefore assign this band in the Fe⁺-seeded CO₂ clusters as arising from similar intermediate CO₂ molecules that are not coordinated to metal and not on the surface but are instead caged between the surface and core.

In experiments so far on Fe⁺(CO₂)_{*n*} complexes, we have measured spectra for complexes up to $n = 14$. Over the size range $n = 10$ –14, there is no change in the spectrum. It appears essentially like that of $n = 12$ shown in figure 7. In our present configuration, we cannot measure the IR spectra of larger Fe⁺(CO₂)_{*n*} complexes because of the lower ion densities available and the decreased photodissociation efficiency at larger size. The latter problem is presumably caused by the slower unimolecular lifetimes of the larger clusters relative to our instrument time window (2–3 μs) in which dissociation must occur to be detected. Future instrument modifications are planned to extend this time window so that larger complexes can be studied. In any event, this initial study of the IR spectroscopy of Fe⁺(CO₂)_{*n*} complexes has already provided a nice first view of coordination and clustering dynamics around a transition metal cation.

4.2. Mg⁺(CO₂)_{*n*} complexes [109]

Mg⁺(CO₂)_{*n*} complexes have also been studied previously with collision-induced dissociation [31(d)] and with theory [35]. Our group has reported the vibrationally resolved electronic spectrum of the $n = 1$ complex [69] and from this derived its dissociation energy (5100 cm⁻¹). The structure for the $n = 1$ complex was determined to be the linear Mg⁺...O=C=O configuration, due to the charge–quadrupole bonding, in agreement with theory [35]. This system provides a good comparison with the IR spectroscopy done on Fe⁺(CO₂)_{*n*} because the binding energies of the $n = 1$ complexes are almost the same, but the electronic structures around the metal cations are quite different.

IR photodissociation in the Mg⁺(CO₂)_{*n*} complexes proceeds in much the same way as it did for the iron cation complexes, with elimination of one or more whole

CO₂ molecules as the only dissociation channel. Like the iron complexes, dissociation for the small complexes requires high IR laser power, and the smallest ($n = 1$) cannot be dissociated at all with the IR. The IR-REPD spectra measured by elimination of CO₂ are rather broad, as seen for the iron complexes. However, the spectra also improve substantially in quality when these complexes are tagged with argon and the IR-REPD process is measured by the elimination of the argon. The argon-tagged spectra for the $n = 1, 2, 3$ complexes, which all require only a single argon atom, are shown in figure 8 [109].

As seen for the corresponding iron complexes, the vibrational bands in the asymmetric stretch region are measured to the blue from the free CO₂ resonance. This is understandable because both metals are expected to bind in an $M^+ \cdots O=C=O$ configuration, giving linear $n = 1$ complexes. However, the Mg^+ spectra for the $n = 2$ and 3 complexes are quite different from those for $Fe^+(CO_2)_{2,3}$. For the iron complexes, only a single IR band was observed for each of these species, while the magnesium cation complexes both have clear doublets here. As we discussed for $Fe^+(CO_2)_n$ systems, the vibrational modes of the multiligand complexes can be considered as in-phase and out-of-phase combinations of the asymmetric stretch motions on the different ligands. The $n = 2$ complex has two possible motions like this, and the $n = 3$ complex also has two (all three ligands in phase and a degenerate $2 + 1$ out-of-phase motion). If the $n = 2$ complex is all linear like the $Fe^+(CO_2)_2$ complex, only the out-of-phase motion is IR active. However, the observation of two IR bands rules out the all-linear structure. Instead, the structure

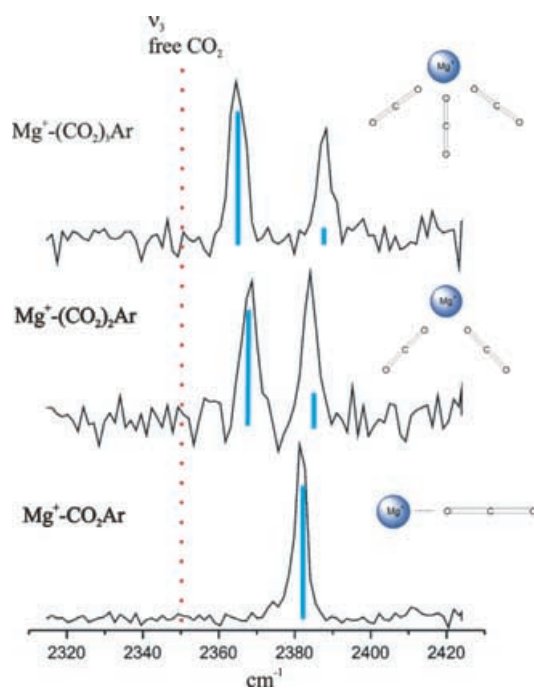


Figure 8. The IR-REPD spectra of $Mg^+(CO_2)_{1,2,3}$ complexes measured with argon tagging and the comparison with the vibrational spectra predicted by density functional theory (DFT). The structures at the right lead to the vibrational bands predicted, which are in excellent agreement with the measured spectra.

must be bent, somewhat like a water molecule, so that both the in-phase and the out-of-phase modes are IR active. Likewise, the $n = 3$ complex must be non-planar (i.e. trigonal pyramid) to have two IR-active modes in this region.

Figure 8 also shows the structures calculated by DFT (B3LYP functional) for the $n = 1, 2, 3$ complexes and the blue bars indicate the vibrational bands predicted for these calculated structures [109]. As shown, the bent structure is indeed predicted for the $n = 2$ complex, as is the trigonal pyramid structure for $n = 3$. The harmonic vibrations calculated initially are scaled using the vibrations of the free CO_2 calculated at this same level of theory. As shown, these scaled vibrations are in excellent agreement with the experiments. The number of IR bands observed and the quantitative agreement with the vibrational frequencies calculated, then, confirm that the $n = 2$ complex is bent and the $n = 3$ is non-planar.

It is therefore interesting to consider why the small CO_2 complexes with Fe^+ have symmetric structures and those with Mg^+ have more asymmetric structures. The symmetric structures seen for the iron system are understandable if the ligands spread out around the metal, minimizing ligand–ligand repulsion. CO_2 molecules beside each other would have opposing quadrupole moments, and this is unfavourable. Indeed, the dimer is well known to have the staggered parallel structure for this reason [125–128]. So, the magnesium complex structures with ligands on the same side of the metal are surprising. Bauschlicher and co-workers actually predicted this effect theoretically before it was observed and explained it in terms of the high polarizability of the Mg^+ valence $3s^1$ electron [35]. When the first CO_2 ligand binds to Mg^+ , it induces a back-polarization on this electron cloud, which results in a lobe of electron density protruding out the back side of the metal. The second and subsequent ligands avoid this negative region and bind on the same side of the metal as the first. We have recently found a similar effect in both the IR spectra of and the theoretical calculations on $\text{Al}^+(\text{CO}_2)_n$ complexes [110], where the valence $3s^2$ configuration also leads to a high metal polarizability. If this same-side ligand addition theme continues, larger complexes of both Mg^+ and Al^+ would eventually look like CO_2 clusters with metal ions imbedded in their surface.

Those familiar with conventional inorganic chemistry often ask why we have studied carbon dioxide systems instead of metal carbonyl complexes with various transition metal ions. However, we cannot study carbonyls at present because of the tuning range of our IR laser. Metal carbonyls usually have C–O stretches that fall in the region below 2000 cm^{-1} [135] where our OPO does not work. We hope to do such experiments on carbonyls in the future with new techniques for the generation of lower frequency IR radiation.

4.3. $\text{Ni}^+(\text{C}_2\text{H}_2)_n$ complexes [111, 136]

Acetylene molecules have C–H stretch vibrations that fall within the tuning range of our OPO laser system. Acetylene is a prototype ligand for organometallic complexes made by conventional synthesis [137], and it has a rich history as an adsorbate on single-crystal metal surfaces where it undergoes a fascinating variety of chemistry [138]. Metal cation–acetylene complexes have been studied in gas phase ion chemistry [24, 25, 29, 31], and selected monoligand complexes have been studied with electronic photodissociation spectroscopy [77, 83(b)]. Theory has investigated the π bonding that occurs with various transition metal ions bonded to acetylene or ethylene [38]. IR spectroscopy has been applied in conventional organometallic acetylene complexes [139] and to unsaturated complexes produced in rare gas

matrices [140–142]. The C–C stretch region is most often studied in these experiments because of its significant oscillator strength and its sensitivity to the chemical interaction with metal. According to the standard Dewar–Chatt–Duncanson model of metal π bonding [143] that applies for acetylene, ethylene and other related species, there is both σ donation of electron density from the acetylene π cloud into empty metal d orbitals and π back-bonding that transfers metal d electron density into the π^* antibonding orbitals on acetylene. Both effects contribute to weaken the π bonding in the ligand, which has the effect of lowering the framework vibrational frequencies compared with their values in free acetylene. This effect is most often measured in the C–C stretch region (1974 cm^{-1} [116]), but this lies below the tuning range of our OPO laser system. The C–H stretches of acetylene (symmetric, 3374 cm^{-1} ; asymmetric, 3289 cm^{-1} [116]) should also be shifted to lower frequencies by metal π bonding, and these are the modes that we probe here. We chose nickel–acetylene complexes for our initial study in this area because of the interesting chemistry known for nickel systems in conventional organometallic chemistry [144].

The bond energy estimated for $\text{Ni}^+(\text{acetylene})$ is about $12\,200\text{ cm}^{-1}$ [38(b)], indicating that these molecules will be difficult to dissociate in the IR, even with the higher frequencies employed in the C–H stretching region. Consistent with this, we find that IR photodissociation is quite difficult, especially for the $n = 1$ and 2 complexes. Beginning with the $n = 3$ complex, intact acetylene molecules are eliminated by photodissociation, but the IR-REPD spectra obtained by acetylene loss are broad. However, as discussed before, we are able to improve the quality of spectra substantially by rare gas tagging experiments with argon. Figure 9 shows the spectra measured in this way for the $n = 1$ –3 complexes [136]. The $n = 1$ complex requires three argons before dissociation is efficient. The $n = 4$ complex does not attach argon efficiently, and it fragments rather easily without tagging, so its ‘neat’ spectrum is shown.

As shown in the figure, the spectra for each of the $\text{Ni}^+(\text{C}_2\text{H}_2)_n$ complexes for $n = 1$ –4 appear to the red of the free acetylene vibrations. This is expected, as described above, when the metal ion binds to acetylene in the π configuration. The $n = 1$ complex has two vibrational bands in the C–H stretch region, and it is therefore easy to associate these with the symmetric and asymmetric stretch vibrations of free acetylene. Both modes are red shifted by over 100 cm^{-1} on interacting with the metal ion. Our DFT calculations allow us to confirm the π bonding structure and to assign the vibrations. The lower frequency band that has the much higher intensity is the asymmetric stretch, and the weaker, higher frequency band is the symmetric stretch. In the $n = 2$ complex, we again must consider vibrations of the two acetylene molecules in in-phase and out-of-phase combinations. If the two acetylene molecules are exactly opposite each other in a D_{2h} configuration, then only the out-of-phase symmetric stretch and the in-phase (*cis*) asymmetric stretch would be IR active, and we would expect only two vibrational bands. However, we clearly see three bands. The occurrence of more than two bands indicates either that the structure has lower symmetry or that more than one isomeric species is present. Again, DFT calculations clarify the situation, finding a C_{2v} structure, with the acetylenes in the same plane as the metal ion, but bent slightly away from the D_{2h} configuration. As a result of this bending, all four C–H stretch vibrations (symmetric and asymmetric, in phase and out) are IR active. The two bands seen before for the $n = 1$ complex are both predicted to split into doublets spaced by 4 – 5 cm^{-1} . This is clearly seen for the more intense lower frequency band,

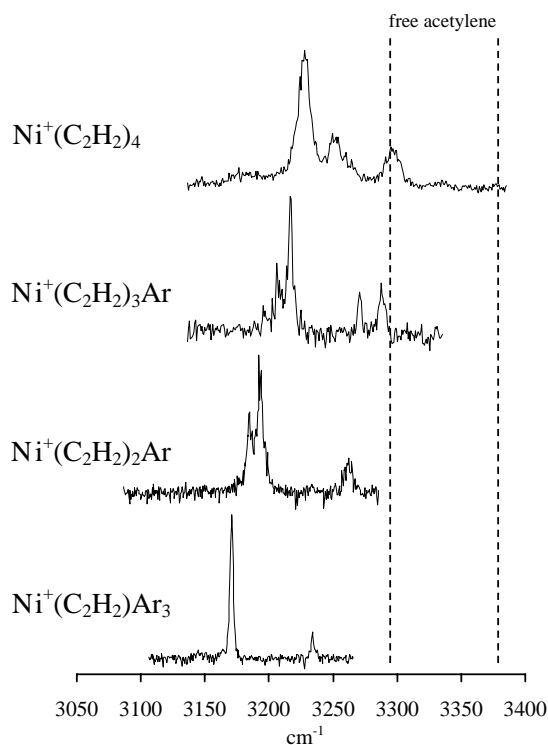


Figure 9. The IR-REPD spectra measured for small $\text{Ni}^+(\text{C}_2\text{H}_2)_n$ complexes in the C–H stretching region. The broken lines show the positions of the asymmetric and symmetric stretch for a free acetylene molecule. The spectra for $n = 1, 2, 3$ complexes are measured with argon tagging, while that of the $n = 4$ complex is measured by C_2H_2 loss.

which is attributed to the asymmetric stretch, but apparently the doublet at the weaker, higher frequency band cannot be resolved. The $n = 3$ complex is predicted to have a C_{2v} structure, rather than the more symmetric D_{3h} , and now three multiplet features are predicted at each of the asymmetric and symmetric band positions. We measure three bands near the asymmetric stretch and two at the symmetric stretch position, and apparently miss one weak band here. The $n = 4$ complex is difficult to argon tag, and so we show its neat spectrum, which is not as sharp as some of the others. Its broad peaks occur in about the same position as the asymmetric and symmetric stretches for the smaller complexes.

Although all these spectra are shifted to the red from the free acetylene resonances, the shift is progressively less with the addition of each subsequent acetylene molecule to the cluster. This is understandable, because average binding energies for multiple ligand additions often decrease with complex size, and the binding energies and vibrational band shifts should follow a similar trend. Even at the $n = 4$ cluster, the vibrational spectrum is still rather simple in appearance. We have interpreted this simple appearance and the smooth progression in band shifts to indicate that the $n = 4$ complex has all four ligands attached to the metal, just as the smaller complexes do [111]. Our photodissociation mass spectra show that elimination often terminates at the $n = 4$ complex, also indicating that it is a relatively

more stable unit. We cannot tell from the spectrum what the structure is around the metal, and we have not done theory yet for this system. However, a tetrahedral configuration of ligands is chemically reasonable for this system and this would be symmetric enough to give a simple vibrational pattern (four IR-active bands are expected and four are detected).

Figure 10 shows that a significant new complexity arises in the vibrational spectrum on going from the $n = 4$ complex to larger ones. The spectra for the $n = 5$ and 6 complexes have some of the same vibrational bands as the $n = 4$ complex, but additional bands are found between these features, particularly in the region near $3260\text{--}3270\text{ cm}^{-1}$ and in the lower frequency region below 3200 cm^{-1} . It is unlikely that clusters this large could have all acetylene molecules coordinated directly to the metal, and so we suspect that these new bands may arise in some way from acetylene molecules in the second layer, i.e. bound only to other acetylenes. Using the same logic that we used previously for CO_2 complexes, we consider that such acetylene molecules may have spectra similar to those of pure acetylene clusters. The IR spectra for acetylene clusters have bands in the $3260\text{--}3270\text{ cm}^{-1}$ region [145], and so we therefore assign the bands seen in this region to the vibrations of external, or ‘surface’, molecules in these metal complexes.

The bands below 3200 cm^{-1} present us with a puzzle. Figure 9 has already shown that there is a steady decrease in the red shift of the vibrations as cluster size increases over the range $n = 1\text{--}4$. At $n = 5$, we see evidence for surface molecules, and we expect a smaller red shift for these, consistent with the bands in the $3260\text{--}3270\text{ cm}^{-1}$ region. However, the other bands seen at $n = 5$ and 6 are more red shifted than those for any cluster except the $n = 1$ species. If these bands represent π -bonded acetylenes, they must suddenly be much more strongly bound than those in the

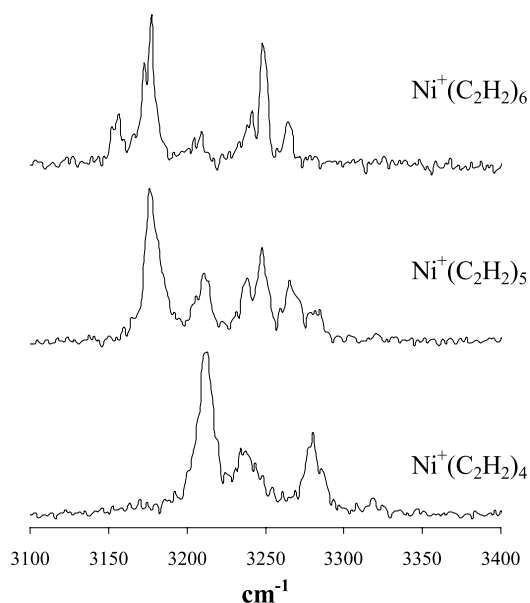


Figure 10. The IR-REPD spectra measured for larger $\text{Ni}^+(\text{C}_2\text{H}_2)_n$ complexes, when $n = 4\text{--}6$. At $n = 5$, lower frequency bands near 3180 cm^{-1} are first observed, which are attributed to a cyclization reaction forming π -bonded cyclobutadiene.

smaller sized clusters, which is difficult to understand. The only reasonable explanation is that the chemical nature of the ligands here has changed so that these bands come from something other than weakly bonded acetylene. In other words, these bands suggest that an intracuster reaction or rearrangement of some sort has occurred.

Acetylene can react in several ways that might explain an intracuster reaction or rearrangement. On metal surfaces it can couple to form benzene, or it can isomerize to form vinylidene [138]. However, both of these species have C–H vibrations that are well known to lie below 3100 cm^{-1} [138]. Acetylene in organometallic chemistry is also known to undergo the Reppe cyclization reaction, which produces cyclo-octatetraene [137, 144], but cyclo-octatetraene also has C–H vibrations near 3000 cm^{-1} . To generate vibrations in this higher frequency region requires smaller, stiffer molecules. Two other candidates are possible from the known cyclization chemistry of acetylene. The metal may be incorporated into a ring via di- σ bonding, to form a metalla-cyclopentadienyl complex. These are known both in organometallic chemistry [137, 144] and in surface science studies on transition metals [146] and silicon [147]. IR spectroscopy studies of organometallics of this kind are rare, but the surface spectroscopy indicates C–H stretching vibrations in the $3030\text{--}3050\text{ cm}^{-1}$ region for this species, which would again be lower than the bands we see. A final possibility is π -bonded η_4 metal-cyclobutadiene complexes, which are also well known in organometallic chemistry [137, 144, 148, 149]. Although cyclobutadiene itself is not stable, the π bonding to the metal produces an overall stable complex. Again, IR spectroscopy studies on such metal-cyclobutadiene complexes are rare, but the existing data indicate that the C–H vibrations of the cyclobutadiene attached to metal occur near 3140 cm^{-1} [148, 149], which is nearly the same frequency found for the isolated butadiene molecule [116]. We see bands near 3170 and 3190 cm^{-1} , which are quite close to this frequency. Therefore, the IR spectrum here agrees best with a metal-cyclobutadiene π complex. To test this hypothesis, we have performed preliminary DFT calculations for the $\text{Ni}^+(\text{C}_2\text{H}_2)_5$ complex [136]. We find that the π -bonded cyclobutadienyl species forms spontaneously and that it has a C–H stretching frequency of 3180 cm^{-1} . This remarkable agreement with our spectrum, and the lack of any other plausible explanation for these new vibrational bands, confirms that an intracuster cyclization to form the π -bonded C_4H_4 species has indeed occurred.

It is interesting to note that the $n = 5$ complex exhibits bands in its spectrum corresponding to surface acetylene molecules and the reaction product. However, there are not likely to be enough acetylenes to have both in the same cluster. The occurrence of both species in this spectrum indicates that there are both isomeric reacted and unreacted species present. It is also interesting to note that the reaction begins just when surface molecules begin to be present. This makes sense, because cyclization reactions are well known to require parallel alignment to be efficient. In the smaller clusters, the acetylene molecules are presumably bound tightly so that their movement into a parallel configuration is not easy. However, when surface molecules are present, their weaker binding should promote facile movement, making it possible to achieve the required parallel alignment with a core molecule. As a final comment, we have recently seen this same reactive behaviour for complexes of $\text{Co}^+(\text{C}_2\text{H}_2)_n$, with an onset at a cluster size of $n = 4$ [150]. These are some of the first examples seen for size-specific intracuster reactions mediated by metal ions where IR spectroscopy is able to identify the reaction product.

4.4. $M^+(\text{benzene})_n$ complexes [112, 113]

Metal–benzene π complexes are classic species in organometallic chemistry [151–153]. These species have been studied extensively with theory [50–54] and they have been examined with a variety of techniques in gas phase ion chemistry [154–156]. Vibrational spectroscopy in the IR has been reported [151–153] and discussed by theory in the context of the perturbation of the free benzene vibrations as they are influenced by charge transfer with the metal [53]. Unfortunately, the IR spectroscopy information previously available for these species has been obtained only for solution or for solid films. There are no high quality data available in the isolated gas phase. The vibrational region studied is usually that of the strongly allowed benzene ring distortional modes and the C–H bending modes, in the 500–1500 cm^{-1} region. By contrast, the higher frequency bands in the C–H stretching region are relatively weak in intensity. Binding energies in these clusters are 2–4 eV [50–54], which are much higher than those for other complexes we have studied, and high-order multiphoton processes are therefore required for photodissociation with IR lasers. Considering all these issues, we have taken a different approach toward the spectroscopy of metal–benzene complexes. On the basis of our recent work using a free electron laser for cluster photoionization studies [157, 158], we recognized that this kind of laser system can provide tunable IR in the 500–1500 cm^{-1} region where the most familiar vibrational modes lie. The free electron laser also has extremely high pulse energies (up to 50 mJ/pulse) and a temporal profile well suited to multiphoton processes. We therefore adapted the cluster molecular beam machine located at the FELIX free electron laser for these ion photodissociation studies. We used ArF laser (193 nm) photoionization of neutral clusters to produce the desired metal–benzene cations, and we isolated these with an ion trap mass spectrometer. Excitation with IR from FELIX produced MPD by loss of intact benzene molecules, and we recorded the wavelength of this process as before. Examples of the resulting spectra are shown in figure 11 for $\text{Al}^+(\text{benzene})$ and $\text{V}^+(\text{benzene})$ complexes. The broken vertical lines indicate the positions of the free benzene vibrations.

As shown in the figure, the vibrations in these monobenzene complexes are shifted with respect to those of the free benzene molecule. The ν_{11} mode which occurs at 673 cm^{-1} in free benzene (out-of-plane C–H bend) is shifted to higher frequency in both metal complexes. The ν_{18} band near 1000 cm^{-1} (in-plane C–H bend) is not shifted significantly in the complexes. Finally, the ν_{19} band which occurs at 1486 in free benzene (C ring distortion) is shifted significantly to lower frequency for the V^+ complex but not for the Al^+ complex. As we have discussed previously [112, 113], these shift patterns are easy to understand. The ν_{11} out-of-plane bend shifts to higher frequency in both complexes. This is attributed to repulsion caused by the presence of the metal over the ring, and this added repulsion drives the frequency higher. By contrast, the in-plane bend near 1000 cm^{-1} is not affected much by the metal. The ν_{19} mode (carbon ring distortion) near 1486 cm^{-1} has been shown by theory to be the most sensitive to the charge transfer character in the π bonding [53]. When there is charge transfer, this is described in the same Dewar–Chatt–Duncanson framework employed for metal–acetylene complexes, with both σ donation and π back-bonding components [143]. The π bonding in benzene is weakened in the same way that it is in metal–acetylene complexes, and consequently the ring-based vibrational mode shifts to lower frequency. This effect is prominent for vanadium which has the required d orbitals, but it is not noticeable for aluminum. We have recently seen similar effects in the spectra for dibenzene

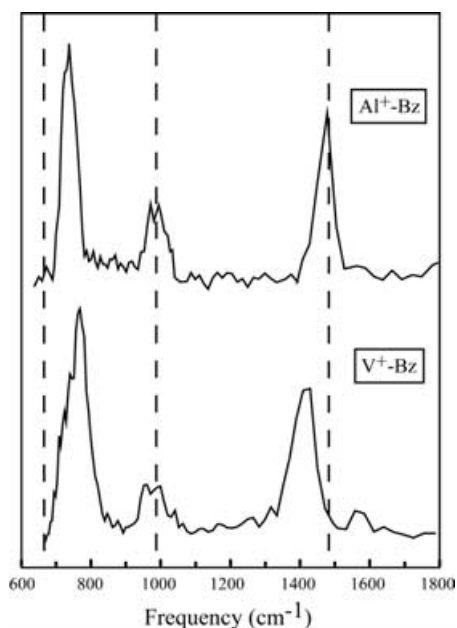


Figure 11. The IR-REPD spectrum measured for $\text{Al}^+(\text{benzene})$ and $\text{V}^+(\text{benzene})$ in the region of the IR-active vibrations of the benzene moiety. This spectrum required the use of the FELIX free electron laser to obtain the lower frequency IR required. The benzene vibrations in the metal complexes occur near to those in the free molecule, but significant shifts are noted. Of particular interest is the ν_{19} vibration on benzene near 1500 cm^{-1} . This mode has a significant shift to the red in the vanadium complex but is hardly shifted at all in the aluminium complex.

sandwich complexes of vanadium [112] and a variety of other first-row transition metal systems [159]. It is now clear that IR photodissociation provides a convenient probe of the spectroscopy of even these strongly bound complexes.

5. Conclusion

As shown in the examples in this review, IR laser photodissociation spectroscopy is now a valuable tool available to probe a variety of metal ion complexes in the gas phase. We find that small complexes are more difficult to dissociate than large ones when excitation occurs in the IR, but multiphoton processes or rare gas tagging methods improve the photodissociation yields significantly. These techniques can also be used to study very strongly bound systems such as metal–benzene complexes. The small molecules that we have studied so far all have vibrational resonances close to those in the corresponding free molecules, but with small shifts that are understandable on the basis of the ligand binding configuration to the metal ion. Ligand vibrational modes that are IR forbidden in the free molecule may become IR active in metal ion complexes, providing more information about the complex structure and bonding. The number of IR bands seen and their shifts compared with free molecule vibrations can be used in coordination with theory to determine the structures of small complexes. Likewise, the occurrence of new bands at larger cluster sizes that have vibrations like those of free molecules allows the identification of surface species that are not coordinated to metal. Coordination numbers have

been determined this way for several metal complex systems. Finally, these studies have found some of the first evidence for intracuster cyclization reactions that couple acetylene to make cyclobutadiene. It is expected that the continued application of this method to other complexes with different metals and ligands will provide a wide variety of information about metal binding, coordination spheres and intracuster reactions in the future.

Acknowledgments

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