

## **Final Report**

"Infrared Spectroscopy of Transition Metal-Molecular Interactions in the Gas Phase"

DE-FG02-96ER14658

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November 15, 2005 to November 14, 2008

## **Executive Summary**

Transition metal-molecular interactions are important in catalysis, in the conversion of crude oil to energetic fuels and chemical feedstocks, and in the solvation and separation of heavy metals from polluted environments. Our research group studies these interactions with model metal-molecular complexes produced and studied under carefully controlled conditions in a molecular beam machine. Various metal cation-molecular ion-molecule complexes have been produced with laser vaporization in a pulsed nozzle source, size-selected with a mass spectrometer and studied with infrared laser spectroscopy. The publications from the work in the present funding period (2005-2008) are indicated below. In this funding period, and other work prior to this, we have studied metal-carbon monoxide complexes in the C-O stretching vibration region, metal-carbon-dioxide complexes near the asymmetric stretch of CO<sub>2</sub>, metal-water complexes in the O-H stretching region, metal-nitrogen complexes in the N-N stretch, metal-acetylene complexes in the C-H stretching region and metal-benzene complexes in the C-H stretching and C-C ring distortion modes. In each system, we investigated the size-dependent photodissociation yield, the number of IR-active vibrations, the shifts in these vibrations that occur on binding to metal compared to the same vibrations in the free molecule, and the relative intensities of different bands. We also computed the structures of these systems and their spectra with density functional theory (DFT). These ground-breaking studies have obtained some of the first information available on the structures of these model complexes, the nature of their vibrational spectra, the variation of electronic spin states on the transition metal ions as different ligands are added to the complex, and the number of ligand or solvent molecules present in the complete metal coordination sphere. This fundamental

information has added many new details to the understanding of transition metal-molecular interactions and new insights into the present capability of computational chemistry to model these interactions.

### Accomplishments in this Funding Period

In the last three years of this ongoing research program, we have focused on metal carbonyl, metal-CO<sub>2</sub>, metal-water and metal benzene complexes. We make these with laser vaporization, mass select the desired complex with a specific number of ligand or solvent molecules, and study these with infrared laser photodissociation in the 700-4000 cm<sup>-1</sup> region using infrared OPO laser systems. Photodissociation spectroscopy is required for these studies rather than simple infrared absorption because of the low densities of ions present in the mass spectrometer. A key aspect of this work is therefore the ligand or solvent molecule binding energy and our ability to cause fragmentation with IR photons. Dissociation energies have been measured for many relevant metal ion complexes by other groups. Table 1 shows typical values for single-ligand complexes, compared to the energy of vibrational fundamentals for different ligands. One-photon IR excitation is not usually energetic enough to cause photodissociation.

Table 1. Fundamental vibrations of small molecules versus typical M<sup>+</sup>-L binding energies.

Molecule	IR Frequency ( $\omega_e$ , cm <sup>-1</sup> )	M <sup>+</sup> -L binding energy (cm <sup>-1</sup> )
CO	2143	5,000-8,000
N <sub>2</sub>	2330	3,000-5,000
CO <sub>2</sub>	$\nu_1, \nu_2, \nu_3 = 1333, 667, 2349$	5,000-7,000
H <sub>2</sub> O	$\nu_1, \nu_2, \nu_3 = 3657, 1595, 3756$	8,000-12,000
C <sub>2</sub> H <sub>2</sub>	sym. C-H=3372, asym. C-H=3244, C≡C stretch=1974, cis-C-H bend=730	9,000-12,000
C <sub>6</sub> H <sub>6</sub>	C-H stretch=3080, ring distortion 1486	15,000-30,000

Bond energies may decrease in larger complexes, but these systems have basically the same problem until the metal coordination is completed. When ligands are present beyond the coordination, they are bound by weaker electrostatic forces and these complexes dissociate readily, providing good IR spectra. To study small complexes

with strong bonding, we attach weakly-bound "spectator" rare gas atoms. To document the effects of tagging, we measure spectra with different numbers/kinds of added atoms (Ar, Ne), and compute spectra for complexes with and without the tag. Vibrations are usually shifted by  $<10\text{ cm}^{-1}$  for Ar and  $<5\text{ cm}^{-1}$  for Ne.

The presence of vibrations in these complexes near those of the corresponding ligands indicates that binding usually occurs without dissociation or insertion chemistry. Comparison of IR spectra to the predictions of theory reveals the most likely geometry for each complex. In some cases, the ground state of the system is in question, and IR spectra confirm which metal electronic or spin state is formed. Abrupt changes in dissociation yield and spectra as complex size increases allows us to identify coordination numbers, as ligands bound to metal have different frequencies than those in outer layers. In complexes with water, we identify the onset of hydrogen bonding, also relevant to coordination numbers and solvation. Finally, in certain complexes containing multiple ligands of CO<sub>2</sub> or acetylene, new vibrational bands indicate the presence of intracuster reaction products. These IR studies are already revealing a fascinating variety of metal-molecular chemistry that could not be seen before.

### *Metal-Carbonyl Complexes*

Metal carbonyl complexes are classic organometallic species and they provide appealing models for CO adsorption on metal surfaces. These continue to be a major focus of our work. However, most carbonyl complexes have vibrations shifted to the red from the free-CO value ( $2143\text{ cm}^{-1}$ ) in the range of  $1700\text{-}2100\text{ cm}^{-1}$ . Until recently, our IR-OPO laser tuning range was limited to  $2000\text{-}4500\text{ cm}^{-1}$ , and operation below  $2100\text{ cm}^{-1}$  was problematic. Therefore, we focused initial studies on carbonyls whose vibrations were expected at higher frequencies. From conventional inorganic chemistry, it was known that "non-classical" carbonyl complexes, having vibrations shifted to the *blue* from free CO, result from metals with full or nearly filled *d* shells. We therefore focused on the noble metals (Cu, Ag, Au, Pt). We obtained spectra for gold and platinum complexes, but had difficulties (low dissociation yields) with copper and silver.

IR spectra for Au<sup>+</sup>(CO)<sub>n</sub> complexes (n=3-7) in the C-O stretching region were interpreted via theoretical computations at the MP2 and CCSD(T) levels using relativistic

core potentials in collaboration with Njegic and Gordon (Iowa State). The  $n=1,2$  complexes and their argon tagged species were too strongly bound to photodissociate, and we could not produce enough neon-tagged species to study. The dissociation yield increased greatly after  $n=2$ , and this complex was enhanced significantly in the mass spectrum, consistent with a coordination of two for this system. The  $n=3-7$  complexes all had a single C-O stretch band shifted  $60-70\text{ cm}^{-1}$  to the blue from free-CO. The  $n=3$  and 4 species had spectra blue-shifted less than that predicted for  $n=2$ , consistent with less favorable three- and four-coordinate structures. Dissociation energies (bracketed with IR photon energies) and spectra were consistent with the predictions of theory, indicating that the  $n=3$  and 4 species have trigonal planar and tetrahedral structures. The strong blue shift in these systems was attributed to efficient  $\sigma$ -donation (due to the positive charge), which polarizes the CO and balances its valence orbital density, with negligible  $\pi$ -back bonding (due to the filled  $d$  shell).

Mass spectra and dissociation patterns for  $\text{Pt}^+(\text{CO})_n$  complexes indicated that the coordination for this system is four. IR spectra for the  $n=4-6$  complexes each had a single band shifted  $\sim 12\text{ cm}^{-1}$  to the blue from free-CO. The spectra for  $n=5$  and 6 were interpreted to arise from the photo-elimination of weakly bound external CO ligands acting essentially as tags rather than ligands. Thus, all three complexes provided the spectrum for  $\text{Pt}^+(\text{CO})_4$ , whose single peak was consistent with the square planar structure predicted previously by theory. The small blue shift was interpreted to arise from offsetting effects of  $\sigma$ -donation (effective) and  $\pi$ -back-bonding (inefficient due to the nearly filled  $d$  shell).

We have expanded studies into the more common carbonyl stretch region with the new IR laser coverage, beginning with the  $\text{Co}^+(\text{CO})_n$  complexes, which would be isoelectronic to neutral iron complexes that form the well-known stable  $\text{Fe}(\text{CO})_5$  complex. We found that the cobalt cation also formed a stable five-coordinate complex, and that the CO stretch frequency in the cation is less than that in the corresponding neutral Fe complex because of the more limited  $\pi$  back bonding in the cation. A second study examined the carbonyls of the vanadium group metals (V, Nb, Ta). A recent theoretical study by the Schaefer group at UGA noted that the  $n=7$  complex for  $\text{V}^+$  has 18 electrons and proposed that this unusual seven-coordinate species would be stable. However, our mass spectrum had a strong enhancement for the  $n=6$  complex (not  $n=7$ ), and the dissociation yield increased significantly after this size. The  $n=6$  and 7 complexes had

similar spectra, each with a single band near  $2100\text{ cm}^{-1}$ , indicating that  $n=7$  represents a  $6+1$  species, with a weakly-bound external ligand. Apparently the predicted seven-coordinate structure is present only in minor concentrations, if at all. Surprisingly, we have recently found that the larger ions  $\text{Nb}^+$  and  $\text{Ta}^+$  do form the seven-coordinate species. Size matters!

In related work, we have re-visited the  $\text{V}^+(\text{CO}_2)_n$  complexes studied previously by our group. These systems had unexpected bands near the asymmetric stretch of  $\text{CO}_2$  that only appeared in larger clusters. We attributed these to insertion chemistry, driven by differential solvation, that produced *oxide-carbonyls*  $[\text{OV}(\text{CO})(\text{CO}_2)_{n-1}]^+$  with the same mass as  $\text{V}^+(\text{CO}_2)_n$ . Using our long wavelength lasers, we have now looked for the carbonyl stretch in these systems. The small complexes had no signal here, but at  $n>6$  a strong band appeared at  $1800\text{ cm}^{-1}$  (Figure 1). To see if this is indeed a carbonyl of a vanadium oxide ion, we made  $\text{VO}^+(\text{CO})_n$  complexes directly, with no  $\text{CO}_2$  present. The carbonyl stretch in these systems occurs at much higher frequency than the  $1800\text{ cm}^{-1}$  band (around  $2200\text{ cm}^{-1}$ ). Apparently, there is an intracluster reaction in the  $\text{CO}_2$  system, but it is not the oxide carbonyl species that we initially suggested. Instead, it appears that this may be a carboxylate or a carbonate species. Theoretical work is now underway to elucidate this fascinating chemistry.

### *Metal-Nitrogen Complexes*

Metal-nitrogen complexes are isoelectronic to carbonyls, but their vibrational shifts and binding energies are generally smaller. We studied  $\text{Nb}^+(\text{N}_2)_n$  species in the  $n=3$ -16 size range. The binding energy in these systems allow elimination of  $\text{N}_2$  ligands on resonance with the N-N stretch after  $n>2$ . The mass spectrum and dissociation behavior indicate that the coordination is six. Each complex has a single N-N stretch band red-shifted from the free- $\text{N}_2$  vibration ( $2330\text{ cm}^{-1}$ ). The shift for  $n=3$  and 4 is  $\sim 70\text{ cm}^{-1}$ , and then it abruptly increases to  $\sim 120\text{ cm}^{-1}$  for larger complexes. DFT explains this, finding that the ground states of the  $n=1$ -4 complexes are quintets, derived from the  $^5\text{D}$  ground state of  $\text{Nb}^+$ , whereas those for  $n>4$  species are triplets. The  $n=4$  complex has a square-planar structure, that for  $n=5$  is nearly a square pyramid, and the  $n=6$  structure is close to octahedral.

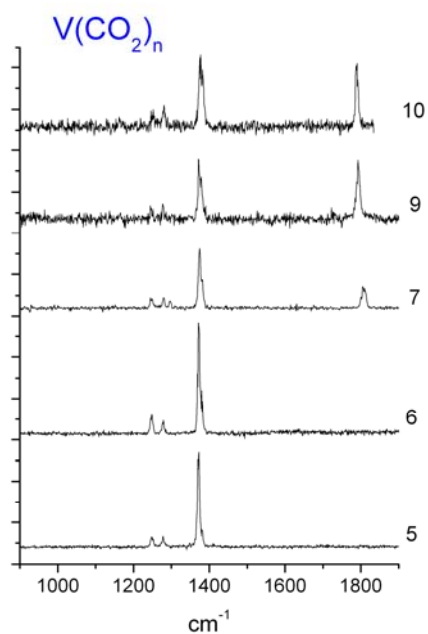


Figure 1. The IR spectra of clusters having the mass of  $V^+(CO_2)_n$ . Bands near  $1200\text{--}1400\text{ cm}^{-1}$  are from the  $CO_2$  symmetric stretch Fermi resonance. The carbonyl from an intraccluster reaction is first seen at  $n=7$ .

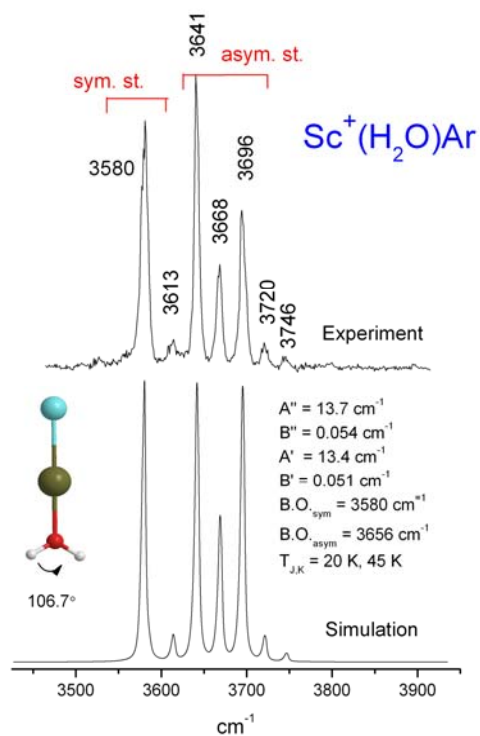


Figure 2. The O-H stretch region for  $Sc^+(H_2O)Ar$ , showing the rotational structure and its simulation.

## *Metal-Water Complexes*

Metal ion-water complexes provide models for cation solvation, and our studies in the O-H stretching and hydrogen bonding region have been extremely informative. In a systematic study, we have measured new IR spectra for  $M^+(H_2O)_n$  species of all the first-row transition metals as well as for the noble metals Cu, Ag and Au. For many of these, we have measured only the small complexes ( $n < 5$ ) with argon tagging. For selected systems (V, Co, Ni) we have measured spectra up to  $n = 25-30$ , documenting the onset of hydrogen bonding and the development of hydrogen bonding networks.

Cation binding to water (usually in a  $C_{2v}$  structure) induces strong perturbations on its infrared spectrum. Both O-H stretches are shifted to the red compared to the symmetric ( $3657\text{ cm}^{-1}$ ) and asymmetric stretches ( $3756\text{ cm}^{-1}$ ) in free water, in much the same way that CO vibrations are red-shifted. The highest occupied orbitals on water associated with the lone-pair electrons have bonding character, and polarization by the metal shifts this electron density, weakening the O-H bonding. The IR bands also have dramatically altered intensities. In isolated water, the asymmetric stretch is 18 times more intense than the symmetric stretch, but these two vibrations have comparable intensities in all of our cation-water spectra. Cation polarization of the dynamic dipole of water enhances the intensities of both vibrations, but the symmetric stretch is more in line with the dipole and experiences a greater effect. Another characteristic of many cation-water complexes is an expanded H-O-H bond angle. In some systems, tagging with a single argon atom is sufficient to obtain the spectrum. If this atom binds on the  $C_2$  axis opposite water, only the light hydrogens rotate about this axis, and K-type rotational structure can be resolved for the asymmetric stretch band. Analysis of this structure provides an estimate of the H-O-H bond angle. We have obtained such data for mono-water complexes with  $Sc^+$ ,  $V^+$ ,  $Cr^+$  and  $Ag^+$ . The simulation of the spectrum for  $Sc^+(H_2O)Ar$  (Figure 2) requires two rotational temperatures,  $T_{J,K} = 20, 45\text{ K}$ , and the estimated H-O-H angle is  $106.7^\circ$ , compared to  $104.7^\circ$  for free water.

Surprisingly, these structural and spectral perturbations do not correlate with the strength of the  $M^+-OH_2$  bond. Instead, subtle details of electronic structure,  $d$ -orbital occupation, cation size and bonding distance, etc. lead to interesting patterns across the first row. We are presently analyzing these data and their trends via DFT computations to complement our experiments. DFT reproduces the vibrational shifts (after scaling) and

intensity patterns, but fails to account for the magnitude of the H-O-H bond angle expansion in these systems. To investigate this more thoroughly, we initiated a collaboration with Allen, Schaefer and coworkers. We employed full anharmonicity in the computed spectrum for  $V^+(H_2O)Ar$  to investigate the role of large amplitude zero-point motion in the bending coordinates on the rotational constants and apparent H-O-H angle. Bending does contaminate the *A* rotational constant, making the H-O-H angle appear to be greater than it really is, but nevertheless significant angle expansion does occur.

We have studied multi-water complexes for several transition metals to explore coordination numbers and the development of hydrogen bonding. Hydrogen bonded O-H stretches usually occur in the 3200-3500  $cm^{-1}$  range, strongly red-shifted from the free-OH vibrations. We find in many  $M^+(H_2O)_n$  systems that the IR spectrum contains only free-OH vibrations up to a certain cluster size, and then all larger sizes have hydrogen bonding bands. This onset, which occurs at  $n=3$  for  $Cu^+$ ,  $n=4$  for  $Co^+$ ,  $Ni^+$  and  $Zn^+$ , and  $n=5$  for  $V^+$  (see Figure 3), is direct evidence for water molecules in the second solvation sphere. The coordination numbers for these singly charged cations in the gas phase are less than those for the corresponding multiply charged ions that are normally found in solution. Another aspect of multiple-water complexes is the nature of the bands in the free-OH region. The symmetric stretch band drops out of the spectrum gradually as cluster size increases; larger clusters have more extensive hydrogen bonding, and it is less likely that two O-H's remain unhindered on the same water molecule. The spectrum evolves gradually in all these systems to a tight doublet band at the position of the asymmetric stretch. In large systems, this free-OH vibration can only occur for water molecules on the surface of the cluster, remote from the metal cation. The doublet comes from the slightly different environment of water molecules that are fully (except for one free-OH) versus partially coordinated. Surprisingly, the doublet spacing varies for  $M^+(H_2O)_n$  clusters with different metal ions. Even in the size range up to 25 water molecules, slightly different inductive effects from the central metal ion are noticeable at the surface of the cluster.

Until recently, our cation-water studies investigated only singly charged complexes, although the charge states in solutions are usually higher than this. Unfortunately, multiply charged metal ion complexes are much more difficult to produce in the gas phase. In the asymptotic limit, many complexes between a dication and a water molecule are

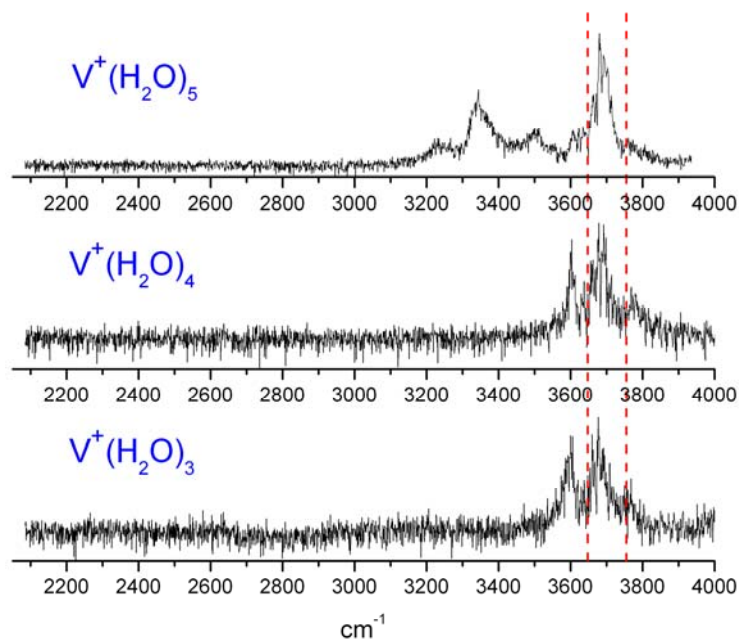


Figure 3. IR spectra for  $V^+(H_2O)_n$  ( $n=3,4,5$ ) showing the onset of hydrogen bonding bands at  $n=5$ . The dissociation yield also improves, indicating the presence of a more weakly bound external molecule.

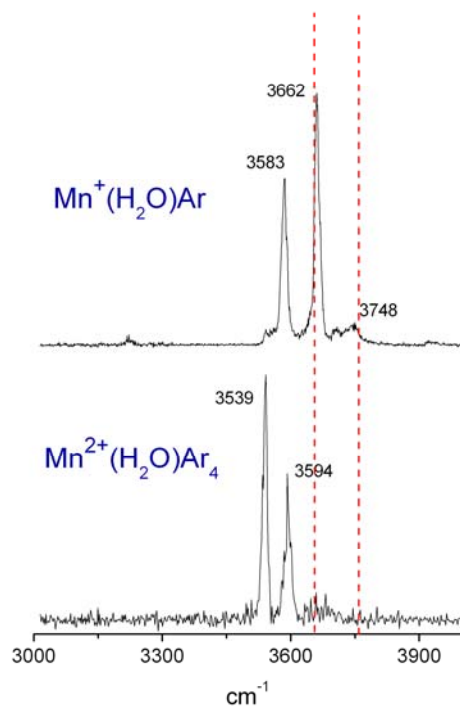


Figure 4. IR spectra for  $Mn^+(H_2O)Ar$  versus  $Mn^{2+}(H_2O)Ar_4$  showing the extra red shift and relative intensity changes for the dication. The red lines show the positions of the bands for isolated water.

“unstable” with respect to charge transfer, because the second ionization potential (IP) of the metal atom is greater than the first IP of water (12.6 eV). A similar problem affects higher charge states. However, unstable complexes may be stabilized by the strong Columbic attraction which dominates at short bonding distances. The critical consideration is how the ions are produced relative to the location of the curve crossing between the  $M^{2+} + H_2O$  and  $M^+ + H_2O^+$  potentials. We have previously shown that multiply charged complexes can be produced with laser vaporization. We have recently been able to produce these ions in greater densities and to argon-tag them, allowing new IR spectroscopy experiments. Williams and coworkers at UC-Berkeley have reported IR spectra for larger ( $n > 5$ )  $Ca^{2+}(H_2O)_n$  (asymptotically stable) and  $Cu^{2+}(H_2O)_n$  (unstable) complexes produced by electrospray ionization, but there is no other data in this fascinating new area. We now have obtained spectra for  $M^{2+}(H_2O)Ar_n$  complexes, for  $M=Cr, Sc$  and  $Mn$ . Figure 4 shows a comparison of the IR spectra for  $Mn^+(H_2O)Ar$  and  $Mn^{2+}(H_2O)Ar_4$ . Because of the greater binding energy, the dication requires tagging with more argons before photodissociation can be observed. As shown, the O-H vibrations shift more to the red and the symmetric stretch intensity is even greater for the dication species. We have detected K-type rotational structure for  $Cr^{2+}(H_2O)Ar_n$  and  $Sc^{2+}(H_2O)Ar_n$  complexes from the internal rotation of water relative to the rest of the cluster. The apparent H-O-H bond angle expansion is also greater in these dications than it is for the corresponding singly charged ions. Much remains to be done to analyze these data, but we are excited by the new prospects here.

### *Metal-Acetylene Complexes*

$\pi$ -complexes are well known in organometallic chemistry, but there are few examples of spectroscopy for these systems in the gas phase. In previous work, we studied the mono-acetylene complexes (tagged with argon) for several first-row transition metal ions to document the trends in these spectra. In the present funding period, we studied larger metal-acetylene complexes of the form  $M^+(C_2H_2)_n$  for nickel, cobalt and copper. Nickel is used as a catalyst with acetylene to make benzene, and we wanted to probe the possibility of acetylene coupling reactions in ion complexes. For  $Ni^+$ , we obtained spectra in the C-H stretching region for the  $n=4-8$  complexes in the acetylene

elimination channel, and we also studied the  $n=1-3$  complexes with argon tagging and the  $n=1$  species with neon tagging. We found that the coordination is complete with four acetylene ligands. Comparing to the predictions of DFT calculations, structures were determined for the  $n=1-4$  species. All were  $\pi$  complexes, but lower symmetries were preferred for the  $n=2$  (near  $C_{2v}$  with ligands puckered to one side) and  $n=3$  (propeller) systems. The  $n=4$  complex had near-tetrahedral symmetry. New strongly red-shifted vibrational bands detected in larger clusters fell at the position expected for the cyclobutadiene coupling product predicted by theory, but additional calculations predicted a band at about the same position for an unreacted isomer with a C-H in a hydrogen bond with the  $\pi$ -cloud of another acetylene. Thus, the presence/amount of cyclization chemistry is presently un-resolved. New experiments in the far-IR (see below) are expected to be useful in this regard. Similar studies on cobalt complexes found a coordination of three and the same strongly red-shifted band in the larger clusters.

### *Metal-Benzene Complexes*

Metal-benzene  $\pi$ -complexes are well known in organometallic chemistry. In previous work, our group has reported some of the first infrared spectroscopy for metal ion-benzene complexes in the fingerprint region of the spectrum using the free electron laser (FEL) and in the C-H stretching region using our OPO laser systems. DFT calculations in coordination with this work suggested the intriguing possibility that binding to transition metal ions could distort the benzene moiety away from planar, and that the degree of distortion would vary with the electronic state of the metal. Our data for  $V^+$  and  $Ni^+$  mono- and di-benzene complexes in the C-H region was consistent with distorted structures, but the band patterns were not completely definitive. In the case of vanadium, the ground states predicted by DFT were triplets for the mono- and di-benzene complexes, but spectra in the C-H stretch region were consistent with quintet spin states for both complexes. Spectra in the fingerprint region should be more informative about ring distortion and spin states, but the FEL data had such poor resolution that it was inconclusive. We have recently employed our extended range OPO system to probe the fingerprint region for argon tagged  $V^+(\text{benzene})$ . A preliminary scan (Figure 5) shows that the ring distortion band near  $1400\text{ cm}^{-1}$ , which was a broad single peak in the FEL data, is

now resolved into a doublet. This confirms that the spin is indeed a quintet, and shows that DFT finds the wrong ground state for this complex.

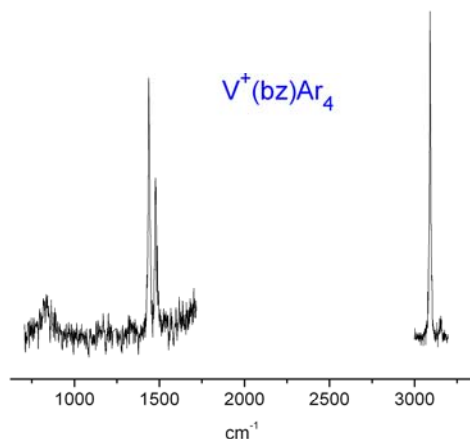


Figure 5. The IR spectrum of  $V^+(\text{benzene})Ar_4$  in the C-H and fingerprint region.

### *Experiments at the Advanced Light Source*

In a collaboration with the group of Steve Leone, we have joined cluster experiments at the Chemical Dynamics Beamline of the Advanced Light Source (ALS) at Lawrence Berkeley National Lab. The Leone group had constructed a beam machine with a high repetition rate laser vaporization source to couple to the quasi-continuous vacuum UV output of the ALS. We teamed up to optimize the source and improve its output. With the improved source, we measured ionization thresholds for carbon clusters up to 15 atoms in size. Wheeler, Allen and Schaefer in our department computed ionization thresholds for linear and cyclic isomers, which in some cases allowed us to identify the structures of the neutral clusters present. Additional modifications in progress will further improve the machine for VUV-cluster experiments on clusters of other materials.

## Publications Resulting From This Work (2005-2008):

R.S. Walters, E.D. Pillai and M.A. Duncan, "Solvation Processes in  $\text{Ni}^+(\text{H}_2\text{O})_n$  Complexes Revealed by Infrared Photodissociation Spectroscopy," *J. Am. Chem. Soc.* **127**, 16599 (2005).

R.S. Walters, E.D. Pillai, P.v.R. Schleyer and M.A. Duncan, "Vibrational spectroscopy of  $\text{Ni}^+(\text{C}_2\text{H}_2)_n$  ( $n=1-4$ ) complexes," *J. Am. Chem. Soc.* **127**, 17030 (2005).

N.R. Walker, R.S. Walters and M.A. Duncan, "Frontiers in the infrared spectroscopy of gas phase metal ion complexes," *New J. Chem.* **29**, 1495 (2005) (invited review).

E.D. Pillai, T.D. Jaeger and M.A. Duncan, "Infrared spectroscopy of  $\text{Nb}^+(\text{N}_2)_n$  complexes: Coordination, structures and spin states," *J. Am. Chem. Soc.* **129**, 2297 (2007).

A.C. Scott, N.R. Foster, G.A. Grieses and M.A. Duncan, "Photodissociation of lanthanide metal cation complexes with cyclooctatetraene," *Int. J. Mass Spectrom.* **263**, 171 (2007).

V. Kasalova, W.D. Allen, H.F. Schaefer, E.D. Pillai and M.A. Duncan, "Model systems for probing metal cation hydration: The  $\text{V}^+(\text{H}_2\text{O})$  and  $\text{V}^+(\text{H}_2\text{O})\text{Ar}$  complexes," *J. Phys. Chem. A* **111**, 7599 (2007).

L. Belau, S.E. Wheeler, B.W. Ticknor, M. Ahmed, S.R. Leone, W.D. Allen, H.F. Schaefer, and M.A. Duncan, "Ionization thresholds of small carbon clusters: Tunable VUV experiments and theory," *J. Am. Chem. Soc.* **129**, 10229 (2007).

J. Velasquez, III, B. Njagic, M. S. Gordon and M. A. Duncan, "IR photodissociation spectroscopy and theory of  $\text{Au}^+(\text{CO})_n$  complexes: Nonclassical carbonyls in the gas phase," *J. Phys. Chem. A* **112**, 1907 (2008).

M.A. Duncan, "Structures, energetics and spectroscopy of gas phase transition metal ion-benzene complexes," *Int. J. Mass Spectrom.* **272**, 99 (2008) (invited review).

P. D. Carnegie, B. Bandyopadhyay and M.A. Duncan, "Infrared spectroscopy of  $\text{Cr}^+(\text{H}_2\text{O})$  and  $\text{Cr}^{2+}(\text{H}_2\text{O})$ : The role of charge in cation hydration," *J. Phys. Chem. A* **112**, 6237 (2008) (letter).

J. Velasquez and M. A. Duncan, "IR photodissociation spectroscopy of gas phase  $\text{Pt}^+(\text{CO})_n$  ( $n=4-6$ ) complexes," *Chem. Phys. Lett.* **461**, 28 (2008).

A.M. Ricks and M.A. Duncan, "IR spectroscopy of  $\text{Co}^+(\text{CO})_n$  complexes in the gas phase," *J. Phys. Chem. A* **113**, 4701 (2009).

P. D. Carnegie, A.B. McCoy and M.A. Duncan, "Infrared spectroscopy and theory of  $\text{Cu}^+(\text{H}_2\text{O})\text{Ar}_2$  and  $\text{Cu}^+(\text{D}_2\text{O})\text{Ar}_2$ : Fundamentals and combination bands," *J. Phys. Chem. A* **113**, 4849 (2009).

P. D. Carnegie, B. Bandyopadhyay and M.A. Duncan, "Infrared spectroscopy of noble metal ion-water complexes,  $\text{M}^+(\text{H}_2\text{O})_n$  ( $\text{M}=\text{Cu}, \text{Ag}, \text{Au}$ ;  $n=1,2$ )" *J. Phys. Chem. A*, to be submitted.

P. D. Carnegie, B. Bandyopadhyay and M.A. Duncan, "Trends in cation hydration of the first-row transition metals revealed with infrared spectroscopy," *J. Phys. Chem. A*, to be submitted.

J. Velasquez, B. Bandyopadhyay and M. A. Duncan, "IR photodissociation spectroscopy and theory of  $\text{Au}^+(\text{CO}_2)_n$  Complexes," *J. Phys. Chem. A*, to be submitted.

## Invited Lectures Resulting From This Work (2005-2008):

"Infrared Photodissociation Spectroscopy of Cation-Molecular Complexes," *Departmental Seminar*, University of Pittsburgh, February 2005.

"Infrared Photodissociation Spectroscopy of Cation-Water Complexes," *Symposium on Size-Selected Clusters*, Brand, Austria, February 2005.

"Photodissociation of Cation-Molecular Complexes, Carbon Clusters and Silicon Carbide Clusters," *Departmental Seminar*, Institute of Physical Chemistry, University of Basel, Switzerland, March 2005.

"Infrared Photodissociation Spectroscopy of Cation-Water Complexes," *National Meeting of the American Chemical Society*, San Diego, CA, March 2005.

"Infrared Photodissociation Spectroscopy of Cation-Molecular Complexes," *Physical Chemistry Seminar*, University of Illinois, April 2005.

"Infrared Photodissociation Spectroscopy of Cation-Molecular Complexes," *Physical Chemistry Seminar*, Ohio State University, April 2005.

"Infrared Photodissociation Spectroscopy of Cation-Molecular Complexes," *National Meeting of the American Chemical Society*, Washington, DC, August 2005.

"Infrared Photodissociation Spectroscopy of Cation-Molecular Complexes," *28<sup>th</sup> International Symposium on Free Radicals*, Leysin, Switzerland, September 2005.

"Infrared Photodissociation Spectroscopy of Cation-Molecular Complexes," *Physical Chemistry Seminar*, University of Utah, October 2005.

"Infrared Spectroscopy of Cation-Molecular Complexes," *Chemical Dynamics Seminar*, Advanced Light Source, E.O. Lawrence Berkeley National Laboratory, November 2005.

"Photodissociation and Infrared Spectroscopy of Mass-Selected Metal-Containing Clusters," *Physical Chemistry Seminar*, Penn State University, December 2005.

*Frontiers in Spectroscopy Lecture Series: 1) "Electronic Photodissociation Spectroscopy of Cation-Molecular Complexes," Department of Chemistry, Ohio State University, February, 2006.*

*Frontiers in Spectroscopy Lecture Series: 2) "Development of the Laser Vaporization cluster Source," Department of Chemistry, Ohio State University, February, 2006.*

*Frontiers in Spectroscopy Lecture Series: 3) "Infrared photodissociation Spectroscopy of Cation-Molecular Complexes," Department of Chemistry, Ohio State University, February, 2006.*

"Infrared Photodissociation and Spectroscopy of Gas Phase Metal Clusters," *Chemistry Departmental Seminar*, Florida State University, February 2006.

"Infrared Photodissociation and Spectroscopy of Gas Phase Metal Clusters," *National Meeting of the American Physical Society*, Baltimore, MD, March 2006.

"Infrared Photodissociation and Spectroscopy of Gas Phase Metal Clusters," *Physical Chemistry Seminar*, Emory University, April 2006.

"Infrared Photodissociation and Spectroscopy of Gas Phase Metal Clusters," *Departmental Seminar*, University of Mississippi, April 2006.

"Photodissociation and Infrared Spectroscopy of Metal Containing Clusters," Tokyo Institute of Technology, Japan, May 2006.

"Photodissociation and Infrared Spectroscopy of Metal Containing Clusters," RIKEN National Laboratory, Tokyo, Japan, May 2006.

"Infrared Photodissociation Spectroscopy of Cation-Molecular Complexes," *Retirement Symposium honoring Professor Naohiko Mikami*, Tohoku University, Sendai, Japan, May 2006.

"Vibrational Spectroscopy of Hydrogen Bonding Interactions," *Gordon Research Conference on Vibrational Spectroscopy*, New England College, Biddeford, ME, July 2006.

"Infrared Spectroscopy of Cation-Molecular Interactions," *Gordon Research Conference on Atomic and Molecular Interactions*, Colby-Sawyer College, New London, New Hampshire, July 2006.

"Infrared Spectroscopy of Cation Solvation in Water," *Telluride Conference on the Molecular Aspects of Solvation*, Telluride, CO, August 2006.

"Infrared Spectroscopy of Cation-Molecular Interactions," *Roger Miller Memorial Symposium*, University of North Carolina-Chapel Hill, October 2006.

"Infrared Spectroscopy of Metal Cation-Molecular Complexes," *FEL Workshop: Horizons in Vibrational Spectroscopy with Free Electron Lasers*, Schloß Ringberg am Tegernsee, Bavaria, Germany February 2007.

"Infrared spectroscopy of cation-water clusters: The role of argon tagging and deuteration," *National Meeting of the American Chemical Society*, Chicago, IL, March 2007.

"Infrared spectroscopy of cation-water networks," *National Meeting of the American Chemical Society*, Boston, August 2007.

"Infrared spectroscopy of cation-molecular complexes: From metal coordination and solvation to carbocations," *Chemistry Department Seminar*, Colorado State University, October 2007.

"Infrared spectroscopy of cation-molecular complexes: From metal coordination and solvation to carbocations," *Chemistry Department Seminar*, University of Colorado-Boulder, October 2007.

"Infrared spectroscopy of cation-molecular interactions in the gas phase," U.S. Department of Energy, Condensed Phase and Interfacial Science Program Contractor's Meeting, Warranton, VA, October 2007.

"Infrared spectroscopy of cation-molecular complexes: From metal coordination and solvation to carbocations," *National High Field Magnetic Lab*, Florida State University, November 2007.

"Infrared spectroscopy of cation-molecular complexes: From metal coordination and solvation to carbocations," *CLIO Free Electron Laser User's Group Symposium*, Paris, France, December 2007.