INFRARED PHOTODISSOCIATION INVESTIGATIONS OF METAL CARBONYL SYSTEMS IN THE GAS PHASE

by

JOSE VELASQUEZ, III

(Under the Direction of Michael A. Duncan)

ABSTRACT

A brief survey of the history of metal carbonyls and their study is provided, and the methods for generating and studying metal containing species in the gas phase are discussed. In the work presented, gas phase metal ion-ligand complexes are generated with a laser vaporization/supersonic expansion source and studied with infrared photodissociation spectroscopy. Specifically, the atomic metal ion-carbonyl interactions of Au⁺ and Pt⁺ with CO and Mg⁺, Al⁺ and Ca⁺ with the organic carbonyl acetone are studied. These complexes' mass spectra and IR photodissociation breakdown patterns give clues about their gas phase coordination number. Metal carbonyl interactions are usually interpreted with the famous Dewar-Chatt-Duncanson (DCD) model. In conjunction with calculations, when available, the IR spectra of these complexes are used to understand the binding interaction and structure. Complexes of Au⁺(CO)_n, n = 3-6 fall under the heading of "nonclassical" metal carbonyls, as evidenced by their vibrational spectra which show shifts of 60-70 cm⁻¹. These complexes have highly symmetric structures as suggested by the single peaks in their IR spectra. Complexes of Pt⁺(CO)_m, n = 4-6, demonstrate only slightly blue shifted spectra of ~ 10 cm⁻¹, and the interaction is suggested to be more of an offsetting synergy in the bonding motifs of the DCD model. In agreement with the previous work of Armentrout and coworkers, our findings indicate that gas phase platinum cation has a preferred coordination number of four that is near square planar. Complexes of M^+ (acetone), M = Mg, Al and Ca, demonstrate classical red-shifted behavior due to their binding to the carbonyl oxygen. The shift each complex displays relative to free acetone can be interpreted in light of the metal's ionic radius Both the Mg⁺ and Ca⁺ complexes have unanticipated doublets in their spectra. These doublets are interpreted as being Fermi resonances with the help of density functional theory. The three studies reported here were aimed at understanding the fundamental interactions of organometallic systems with relevance to inorganic and biochemistry.

INDEX WORDS: Gas phase, Laser vaporization, IR photodissociation, Infrared, Gold, Platinum, Magnesium, Aluminum, Calcium, Carbon monoxide, Carbonyl, Acetone, Classical carbonyl, Nonclassical carbonyl

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SYSTEMS IN THE GAS PHASE

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DEDICATION

I dedicate this work to my father and grandfather, who are sorely missed but still dearly loved. They still empower and embolden me.

"Let's go, let's go, let's go!" -Jose Velasquez, II

"Why sure"

-Joseph Hafford Akens

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There are a few people who deserve special acknowledgement: my parents, my grandparents and my wife. They've all been influential and so supportive of my personal goals and accomplishments through the various stages of my life. They truly are a gift from the Supreme.

There are a multitude of others who have contributed to my achievement, and they know who they are.

"We can't define anything precisely." -Richard P. Feynman's Lectures on Physics, Volume I, 8-2

"The only thing that we know is that we know nothing and that is the highest flight of human wisdom." -Lev Nikolaevitch Tolstoi

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CHAPTER 1

INTRODUCTION

Metals make up the majority of known elements, and they exhibit significant variations in chemical and physical properties. They may naturally be found in the earth's crust and core and in all bodies of water. Moreover, metal atoms and ions are introduced to the atmosphere through the ablation of meteors.^{1, 2} In nature, most metals exist in one of several possible charge states due to their inherently low ionization potentials, but of course some are found as both economically and historically important neutrals. At a chemical level, metals and their ions may participate in bonding ranging from purely electrostatic to purely covalent, often with a mixture of these interactions. Metals in ionic form can serve to activate biological and enzymatic activity within organisms,³⁻⁵ catalytically affect reactions of industrial scale and importance^{6, 7} and influence the manifold reactions in terrestrial, aquatic and atmospheric environments.

The study of metal ion-ligand complexes is an important cornerstone to understanding the binding, energetics, coordination and solvation of species with biological, catalytic and synthetic importance. For example, in enzymes, the binding of cations often determines structure, specificity and function.⁸ Metals and metal aggregates are thought to provide surfaces for complex reactions in the interstellar medium.⁹ Furthermore, the foundations of much of coordination chemistry and organometallic chemistry rely on neutral and/or ionic metal's interactions with one or more ligands.¹⁰⁻¹²

Metal carbonyl systems form an important class of compounds in industry, inorganic chemistry and surface science. The well-known Fischer-Tropsch mechanism for converting carbon monoxide into usable saturated hydrocarbons relies on carbon monoxide's interaction with a metal surface, notably iron or cobalt.^{6, 10} Additionally, whole sections or chapters of typical inorganic textbooks are devoted to metal carbonyls.¹⁰⁻¹² Carbonyl functional groups form part of the structure of amino acids in proteins to which a metal often binds.^{13, 14} While much of the groundwork for understanding metal carbonyls has been laid, many questions remain. In particular, the contributions of solvent interactions and counterions are not fully understood in terms of the metal carbonyl binding and structure. Moreover, the specific components of the interaction in the binding of a CO molecule or carbonyl functional group to a metal is not clear for gas phase systems, unhindered by counterions and condensed phase media.

This introduction begins with a section surveying metal carbonyl interactions as understood with traditional inorganic models of binding. Then, it will examine our general understanding of gas-phase metal carbonyl systems through various experimental and theoretical studies. Finally, it will examine our understanding of the origins of the behavior of metal carbonyls, specifically related to vibrational shifts in IR spectroscopy. In the subsequent section, we will examine the general methods used to produce gas phase ions, and support the reasons for our method of choice. Finally, we will briefly examine what methods have been used to probe gas phase metal ion-ligand complexes, including a survey of our work using IR spectroscopy to probe metal ion-ligand systems.

1.1 Metal Carbonyl Interactions

The majority of known metals form complexes with CO. Transition metals are widely known to form metal carbonyl complexes, but main group metal- and metalloid-carbonyl complexes do exist.¹⁵ This is remarkable because CO is generally considered a weak Lewis base, and yet it forms strong bonds to metal centers.¹¹ The strong binding of carbon monoxide to transition metals is usually interpreted in light of the 18-electron rule, to which the majority of these complexes adhere.¹⁰⁻¹² According to this principle, carbon monoxide donates two electrons in a dative interaction, and many condensed phase complexes exist which fulfill the 18-electron rule for stability.^{10, 11} Of-

tentimes, the complexes are multinuclear, in which multiple metal atoms are involved, such that all the metals reach this associated level of filled-shell stability. While this orbital-filling principle is a generally observed rule, it is not absolute. A notable exception to the 18-electron rule is $V(CO)_{6}$, which has 17 electrons.¹⁰⁻¹² This neutral example has nearly a full d shell and forms stable complexes, being very close to the 18-electron count.

While the 18-electron rule is a starting point for understanding coordination numbers and structures, there is much theoretical research aimed at a deeper understanding of the interactions of metal carbonyl systems. This work has attempted to improve our understanding of the metal-CO bond, the reasons for its spectral shifts in the infrared and the binding interactions which define these two observables. Frenking and coworkers wrote an excellent review detailing the bonding of transition metal compound with ligands, including CO.¹⁶ Many other papers have probed the bonding in metal carbonyl systems at various levels of theory.^{16-22, 23} Other theoretical work has aimed at understanding the electronic properties of various metal carbonyls.^{24, 25} Thus, theoretical work has paved the way for the enhanced knowledge of metal carbonyl properties, but it is left to experiment to validate theory and make observations. Hence experiments are necessary to test theory and help deepen our understanding of these fundamental chemical systems.

In surface science, carbon monoxide exhibits interesting signature behavior, and it is well known that the C-O stretching frequency depends on its binding motif on a metal surface.⁷ The stretching frequency of free CO is 2143 cm⁻¹.²⁶ For so-called "atop" sites, in which the carbonyl is localized to only one metal atom on the surface, the characteristic frequency observed is in the range 2000-2200 cm⁻¹. However in a bridging configuration, where a single CO molecule spans two metal atoms, the frequency shifts significantly to the red, typically 1850-1900 cm⁻¹. Likewise, for three-fold

binding interactions, a further red shift may be observed as low as 1800 cm⁻¹. In an isolated complex of CO with a metal atom or small metal cluster, the vibrational shifts can tell much about the pre-ferred binding using infrared spectroscopy.

In the condensed phase, metal carbonyl complexes often exist with the metal in a zero oxidation state. However, many ionic metal carbonyl complexes have been synthesized, requiring counterions. Aubke and coworkers have published a number of papers on the generation of ionic metal carbonyl species in the condensed phase and reported their infrared spectra.^{27,35} In relatively recent work, they have generated a number of homoleptic cationic carbonyl complexes of Ir(III),³⁰ Pt(II),^{27,31} Ag(I)³² and Au(I)^{32,35} in fluoro- and super-acid media. They report vibrational shifts and interpret them in light of popular bonding models and condensed-phase interactions. Gas phase spectra of the metal ion carbonyl complexes are important to understand the effects that the superacid solvents and counterions play in these vibrational shifts.

Andrews and coworkers have examined many metal carbonyl systems in frozen, rare gas matrices using infrared spectroscopy.³⁶ They have reported vibrational shifts for nearly all neutral transition metal carbonyl complexes and many anionic transition metal species.³⁶ For cationic metal carbonyls, they have described vibrational shifts in CO complexed to Groups 8,³⁶ 9,³⁶ 10,³⁷ and 11³⁸, ³⁹ transition metals. Other groups have reported vibrational spectra for atomic copper-, silver- and gold-CO as well as gold cluster-CO complexes in frozen matrices.^{40, 41} While the effects of the rare gas matrices can be estimated, it is not entirely clear what changes they induce in the IR spectra of the metal carbonyl species. Clearly, gas phase work is needed to further probe these metal carbonyl interactions. Much gas phase work has been done trying to elucidate the chemistry, binding interactions and structures of ionic metal carbonyl systems using mass spectrometric techniques. Using collision induced dissociation (CID), Armentrout and coworkers have studied a number of metal carbonyl systems and determined their bond energies. In conjunction with theory they have interpreted their findings and reported gas phase coordination numbers for a number of main group and transition metal complexes, including Li^{+,42} Na^{+,42} K^{+,42} Mg⁴³, Pt^{+,44} Cu⁴⁵, Ag^{+,45} Fe^{+,46} V^{+,47} and Cr⁺⁴⁸ complexed to CO.⁴⁸ Using this same technique, Ervin and coworkers have looked at the binding and reactivity in anionic metal carbonyls formed from Group 10^{49, 50} and Group 11^{51, 52} transition metals. While mass spectrometric techniques can provide much information about these gas phase complexes and hint at the bonding, they cannot directly elucidate the structure of these complexes. It is up to spectroscopy to supplement our understanding of these gas phase metal carbonyl complexes.

There have been a number of photoelectron studies of gas phase metal carbonyls. Lineberger reported photodetachment studies of anionic metal carbonyls of Ni and Fe.^{53, 54} Using this same technique, other groups have reported photoelectron spectra of Group 6 and Group 8 metal carbonyls.⁵⁵⁻⁵⁷ Similarly, Wang and coworkers have studied CO on noble metal surfaces using photoelectron spectroscopy.⁵⁸⁻⁶⁰

Metal carbonyl complexes were some of the first systems isolated and characterized with infrared spectroscopy, and according to their vibrational shifts, they are often interpreted in terms of two general labels. Classical metal carbonyls, which describes the bulk of all metal-CO complexes, typically exhibit red-shifted vibrational spectra, decreased C-O bonding and shorter metal-carbon bonds.¹⁰ Conversely, nonclassical metal carbonyls show blue shifted behavior and increased C-O bonding.¹⁰ Typically, nonclassical systems also have increased metal-carbon bond lengths. A salt of

platinum carbonyl was the first complex to be studied, and remarkably it showed a blue shift, which is associated with nonclassical metal carbonyl behavior.⁶¹⁻⁶³ That the bulk of the metal carbonyl species probed in the ensuing century were primarily classical in nature is no surprise, owing to the mechanism used to understand the bonding in these systems. That mechanism is the famous Dewar-Chatt-Duncanson (DCD),^{10, 64, 65} sometimes called the Blyholder bonding scheme,⁶⁶⁻⁷¹ when applied to metal surfaces. These bonding mechanisms have been applied with success to many other metal ligand interactions such as metal water systems.⁷²⁻⁷⁴ In metal carbonyl systems the tendency of CO is to bind end-on through its C terminus, and this binding occurs through two primary contributions. An on-axis σ -type type interaction arises from the dative electron contribution from the ligand to the metal. This is believed to largely determine the bond distance of the metal-ligand complex and is of a more electrostatic charge-dipole nature. This interaction generally causes an increase in vibrational frequency relative to free CO and stronger CO bonding, as discussed below. Additionally, there is a π back-bonding mechanism, often associated with the metal's d electrons, if present. These d electrons contribute electron density into the empty antibonding orbital of the ligand resulting in three primary effects. First, the metal-ligand binding becomes more covalent in nature, as true sharing of electron(s) occurs. Secondly, the ligand bonding becomes weaker, as electron density is donated into the CO antibonding orbitals. Finally, there is usually an apparent vibrational shift in the C-O stretching frequency. It is generally accepted that the back bonding motif is the more important contribution to the binding in metal carbonyl systems.¹⁶

The origin of the relative shift of the vibrational frequency in a metal carbonyl system is largely understood in terms of a DCD mechanism, as mentioned above. All metal carbonyl interactions involve a σ -type donation of electron density from the 5 σ HOMO of CO to the metal, resulting in the dative metal-CO bond. For classical carbonyls, the dominant contribution to the binding

is a covalent back bonding in the 2π * LUMO of CO resulting in vibrational frequencies that are often shifted to much lower values than that in free CO. This effect is seen for the bulk of all transition metal carbonyl systems. However, for metal ions with closed d shells such those in Group 11 (Cu⁺, Ag⁺ and Au⁺) and main group metals which have no d electrons, back bonding is usually inefficient, if present at all.

To study the origin of the vibrational blue shift associated with binding to these metals, Lupinetti and coworkers did a series of computations to elucidate the effects of metal ion binding on the C-O stretching frequency and electron distribution.¹⁸ They determined that the σ -type interaction of all metal-carbonyl systems results in a vibrational blue shift due to the shift of electron density in the molecular orbitals on CO. The bonding molecular orbitals on free CO have a slight polarization on the oxygen end, resulting in an inhomogeneous electron distribution. Upon binding to a metal, the electron density in the C-O bond shifts becoming more homogenous, creating a stronger interaction and resulting in higher vibrational frequencies. In effect, the CO binding becomes more "N2-like" with balanced bonding molecular orbitals. Moreover, when Lupinetti and coworkers computed the effect to vibrational frequency when the cation binds to the oxygen end in CO, the result was a red shift. This is an important finding, because previous suggestions about the blue shift considered its origin to be in the slight antibonding character in the 5σ CO orbital.¹⁶ That idea held that loss of electron density in the 5σ orbital resulted in a stronger CO bond and higher stretching frequencies because of a reduction in antibonding electron density. If this were true, then a cation binding to either end of the CO molecule should result in blue shifted frequencies, and the findings of Lupinetti and coworkers clearly refute this.¹⁸ This σ -type interaction, while not the dominant interaction in classical metal carbonyls, is still clearly the fundamental binding motif which paves the

way for π -type back bonding. Moreover, this electrostatic interaction is present in *all* metal carbonyl complexes, although it is largely offset in *most* systems through the covalent backbonding interaction.

Classical and nonclassical have become general terms used to designate the relative shifts of the vibrational frequency for condensed phase studies. As mentioned above, it is widely accepted that nonclassical metal carbonyl systems have vibrational frequencies that are greater than 2143 cm⁻¹. Classical metal carbonyl systems exhibit vibrational frequencies below this value. However, Strauss and coworkers have challenged this simple distinction based on their theoretical work.^{18, 19} They claim that the definition of classical versus nonclassical should be tied less to the vibrational shifts that CO undergoes when attached to a metal, but rather to the metal-CO bond distance. This is an important idea, because as Strauss and coworkers point out, the counterions and solvent present in condensed phase vibrational spectra can result in significant changes to the back-bonding component in the DCD model.¹⁹ This increased backbonding can result in significantly shorter metal-CO bond lengths, usually associated with classical behavior, but with vibrational shifts that fit the traditional nonclassical description (i.e., to the blue of free CO). As Strauss and coworker discuss, there exists a region where classical and nonclassical behavior collapse into a bonding scheme where the origins of these classifications largely offset one another.¹⁹ In fact, we observe this with gas phase platinum ion carbonyl complexes, as discussed in Chapter 4. The blue shifts we report are minor, ~ 10 cm⁻¹, unlike the clearly nonclassical gold ion-carbonyl complexes which have shifts of 60-70 cm⁻¹. The unpaired electron in Pt⁺ strengthens the covalent interaction with the CO, an interaction that is not possible for the closed shell gold ion. So by standard inorganic definitions,¹⁰ we could argue that platinum cation carbonyl complexes are nonclassical. But until higher level calculations for

this system are available, we can only suggest that the nonclassical and classical motifs in the binding are largely offsetting and the resulting observed blue shift is slight.

The above discussion is for metal-CO interactions, but this dissertation also presents work done for main group metal ions interacting with the organic carbonyl acetone. As discussed later, this interaction is clearly of the classical type with a significant C=O vibrational red shift relative to free acetone. Like the metal-CO systems, the basis for this red shift is the binding interaction between the metal and the carbonyl in acetone. However, in the complexes of $M^+(acetone)$, M = Mg, Al, Ca, the binding is through the oxygen of the carbonyl and not through the carbon. The resulting red shift in vibrational stretches is the result of this interaction, as discussed in detail in Chapter 5. In brief, the lone pair b_2 electrons of the oxygen have slight bonding character. In interacting with the metal ion, the C=O bond is weakened slightly and the vibration shifts to lower frequency. The magnitude of this shift should depend on the size of the metal cation, and arguments are made that support this idea.

In conclusion, the direction and magnitude of the vibrational shifts that we can measure for metal carbonyl systems in the gas phase, in conjunction with theory, can help to elucidate the dominant binding interactions causing these shifts. Metal carbonyl systems serve as convenient laboratories to test high level theory and expand our understanding of the chemical interactions that these organometallic systems undergo. This dissertation aims to shed some light on our understanding of these systems.

1.2 Generation of Gas Phase Metal Ion Complexes

One of the first techniques for synthesizing metallic and molecular ions in the gas phase was electron impact ionization (EI), which is still used today.⁷⁵⁻⁷⁷ This method uses an electron beam to

ionize materials vaporized by an oven or other means. But the EI method has its drawbacks. First, the energetic electrons often cause fragmentation of the ions of interest, which limits this method to the study of relatively strongly-bound systems, as more weakly bound systems do not survive intact. Secondly, the ions that can survive fragmentation may obtain high internal energies from collisions with the energetic electron beam. Such high internal energies can lead to broad spectra that are difficult to decipher. Strategies have attempted to overcome this second drawback by coupling the EI source with a supersonic expansion.⁷⁸⁻⁹² But the main limitation for our work is that the EI process requires starting materials which have a high vapor pressure or low melting point.

Other techniques for generating gas-phase ions include discharge sources,^{60, 76} electrospray sources^{93,105} and Matrix Assisted Laser Desorption Ionization,¹⁰⁶⁻¹¹¹ abbreviated as MALDI. While all of these techniques do offer their advantages for the production of ions in the gas phase, they all generate relatively low ion densities and each presents its own drawbacks. Discharge sources require conductive materials, which limits them for the study of semimetal and nonmetal substances. Moreover, the high electrical fluxes necessary to generate sufficient quantities of metal-containing complexes can lead to hot gas-phase complexes, though coupling the discharge source to a supersonic expansion can help mitigate the complex's high internal energy by transferring it to translational motion. Electrospray sources can produce gas-phase metal ion complexes with metals in their nascent condensed-phase oxidation state, whereas most other techniques produce metal ions in a singly charged state. Electrospray sources start with metal-ligand complexes in solution and introduce them into vacuum via a charged needle electrode inside a glass capillary. But electrospray sources generally yield small quantities of gas-phase complexes that can have high internal energies. MALDI has been effectively used to propel large molecules into the gas-phase and ionize them softly. While this technique is effective, especially for biological samples, it has the added complexity of relying on

a matrix for the generation of gas-phase complexes. Moreover, a MALDI-generated sample can be internally hot.

Laser vaporization has proven to be a viable technique for generating gas-phase clusters and complexes of nearly any solid material.¹¹² Here, a laser is used to vaporize the material directly without the need for heated ovens, capillary delivery systems or matrix compounds. Moreover, this method can produce large ion densities unlike the techniques discussed above. However, laser vaporization used by itself can produce complexes with high internal energies. Coupling the laser vaporization technique with a pulsed nozzle can create a supersonic expansion that effectively generates cold metal complexes in the gas phase.¹¹²⁻¹³⁸ With the supersonic expansion the hot internal degrees of freedom are transferred to translational motion, and the complexes are effectively cooled. Because of its facility for dealing with highly refractory materials, high ion yield, and effective cooling, we employ this technique for all of the studies presented here. The details of how we couple laser vaporization to the pulsed nozzle and implement it in our experiments are outlined in detail in the next chapter.

1.3 The Study of Gas Phase Metal Ion Complexes

Ionic gas-phase metal complex systems have been extensively studied in the past with mass spectrometry. These spectrometric methods have aimed at determining binding energies, coordination numbers, gas-phase reactivities and the thermodynamics for a variety of different metal ion-ligand systems. Collision induced dissociation, radiative association studies and equilibrium mass spectrometry have been used to report metal-ligand binding energies.^{5, 42-48, 131-141, 141, 141, 141, 142, 142-145, 145-159} These mass spectrometric studies can directly correlate reactivity and binding energies with the size of the complex; however, they cannot directly elucidate the structure of such complexes. Spectroscopy is needed to obtain structural information about these gas phase metal-ion complexes.

Traditional direct absorption experiments are generally not feasible for complexes generated with the above mentioned sources, as the gas phase ion densities are simply too low. Even the laser vaporization technique produces ion densities that are below the detection limits of most instruments relying on direct absorption. Thus, alternate means of studying the spectroscopy of gas phase ions were developed. Action spectroscopy relies on an event of the complex related to the resonant absorption of a photon. Both photoionization and photodissociation can be detected efficiently, and monitoring their yields allows a spectroscopist to study a complex through their action.

In earlier work by our group and others, the electronic spectra of small molecules and complexes were studied using dye lasers and UV-visible optical parametric oscillator/optical parametric amplifiers (OPO/OPA). In those studies, the chromophore is usually the metal ion center, which must have an accessible electronic transition within the range of the available light sources. Metal cations such as Mg⁺ and Ca⁺ have convenient p \leftarrow s transitions which permit complexes with these ions to be probed with tunable UV-Vis sources.¹⁶⁰⁻¹⁷⁷ Our group,¹⁶⁰⁻¹⁶⁶ Fuke and coworkers¹⁶⁷⁻¹⁷¹ and Kleiber and coworkers¹⁷²⁻¹⁷⁷ studied these metals bound to molecules such as N₂, CO₂, H₂O, C₂H₂, C₂H₄ and CH₃OH and rare gases such as Ne and Ar. Other groups have made similar measurements on complexes of these ligands with strontium cation.¹⁷⁸⁻¹⁸² The vacuum-UV electronic spectra of Al⁺ bound to single ligands has been similarly investigated.¹⁷⁵ Brucat and coworkers^{113-115, 183-190} and Metz and coworkers¹⁹¹⁻¹⁹⁵ have also examined complexes of transition metals with small molecules. But transition metals are usually inherently reactive, which can result in broad spectra. Furthermore, the primary limitation of electronic photodissociation studies is that only very small systems have sharp spectra. Complexes with multiple ligands often rapidly predissociate upon electronic excitation, which leads to broad, featureless spectra providing limited information.¹⁹⁶

An alternative to electronic photodissociation spectroscopy is zero kinetic energy (ZEKE) photoelectron spectroscopy and its cousin Mass Analyzed Threshold Ionization (MATI).¹⁹⁷⁻²⁰² In ZEKE spectroscopy threshold electrons that are produced are detected, as light from a tunable source photodetaches an electron from an anion or ionizes a neutral complex. Hence this spectroscopy technique can be used to measure the ionization potential of a neutral of the electron affinity of an anion. ZEKE spectroscopy can provide rotationally resolved structure in a spectrum, further elucidating the geometries of a complex's electronic states. MATI is a similar technique where instead of detecting the low energy electrons, the resultant ions are detected and mass analyzed. Since neutral complexes often undergo a significant change in geometry when ionized, an analysis of the Frank-Condon factors is essential to fully understand the neutral/ionic electronic states probed with ZEKE spectroscopy. Wang and coworkers have used photoelectron spectroscopy to study many systems, including gold cluster anions.^{58-60, 110, 111, 203, 204}

Finally, infrared resonance-enhanced photodissociation spectroscopy (IR-REPD) is a relatively recent technique for studying metal ion-ligand complexes in the gas phase. Unlike the electronic spectroscopy methods where the metal center is the chromophore, IR action spectroscopy probes the vibrations of attached ligands. Structural information can be determined directly with the help of theory because the probed complexes are in the ground electronic and vibrational states. Because the photon energies are relatively low, reactions are generally not initiated upon irradiation, however intracomplex reactions have been probed with IR-REPD by our group.^{72, 205} Early work in IR photodissociation spectroscopy used line-tunable CO₂ lasers to study metal ligand systems.²⁰⁶⁻²¹⁴ Due to the inherently small tuning range of these lasers, these studies were limited. However, relatively recent advances in laser technology provide broadly tunable light that can be used to investigate many vibrations. Free electron lasers (FELs) produce tunable IR light spanning 40-2500 cm⁻¹. These devices permit the study of fingerprint IR modes as well as some low-frequency metal-ligand stretches. Indeed many studies of metal ion-ligand complexes, metal cluster ion-ligand complexes and neutral metal carbide and metal oxide systems have been reported by Meijer and coworkers using a FEL.^{70, 215-223} While these devices have opened up a whole new arena for IR spectroscopy, they do present some limitations. Due to the high intensity and inherent nature of the pulse train generated by these FELs, multiple photon absorption is often the mechanism for dissociating strongly bound complexes with the result being broad spectra, often with linewidths that exceed 30 cm⁻¹. For more weakly bound systems, the spectra can be power broadened. Clearly it is challenging to make a detailed spectroscopic analysis with such large observed linewidths. Furthermore, FELs require significant investments in space and cost. Experiments must "go" to the laser, rather than bringing the laser to the experiment as discussed below.

Benchtop OPO/OPA systems are now available which produce tunable IR light in the 2000-4500 cm⁻¹ region with linewidths of less than a reciprocal centimeter. With an additional modification, the tuning range of these basic systems can be extended down to near 700 cm⁻¹. These laser systems have been used to study a variety of gas-phase molecular complexes in numerous laboratories.²²⁴⁻²³³ Lisy and coworkers were the first to use an IR OPO/OPA system to study alkali and alka-line earth metal ion complexes via IR-REPD.⁷⁷ Inokuchi and coworkers have studied similar metal ions complexed to NH₃, H₂O and CH₃OH this way.²³⁴⁻²³⁷ Our group was the first to apply IR-REPD spectroscopy to transition metal ion-ligand complexes.²³⁸ We have used this technique to

study a variety of metal ions complexed to CO_2 ,^{72, 205, 238-242} N_2 ,^{243, 244} H_2O ,^{72, 74} C_2H_2 ,^{245, 246} C_6H_6 ,²⁴⁷⁻²⁴⁹ and CO.²⁵⁰ As mentioned above, more recent developments in IR generation technology have permitted the study of infrared bands below 2000 cm⁻¹.²⁵¹⁻²⁵³ The addition of an AgGaSe₂ crystal to the OPO/OPA allows the benchtop system to produce tunable light down to ~700 cm⁻¹. Using this crystal, we measured spectra for M⁺(acetone) complexes, M = Mg, Al, Ca, near the carbonyl stretch of acetone (1731 cm⁻¹)²⁵⁴, as discussed in Chapter 5. Our IR-REPD studies have allowed us to understand the coordination numbers of metal cations as well determine the structures of M⁺(ligand)_n complexes.

While IR-REPD spectroscopy can lead to the understanding of a gas-phase complex's binding, structure and coordination number, it is not without limitations. First, the metal ion-ligand complex must dissociate on the timescale of the experiment for detectable fragmentation. Energy absorbed by the ligand is vibrationally redistributed throughout the complex. If there is sufficient energy to fragment the molecule upon redistribution (i.e., sufficient energy is deposited into the weakest bond, usually the M⁺-ligand bond), a bond may break and action spectroscopy recorded by way of ligand elimination. For larger complexes with many ligands, less energy is typically required to eliminate a ligand; however, the increased density of states that arises from the large complex translates to slow vibrational redistribution and long lifetimes. Hence, the complex may not fall apart on the timescale of the experiment. Conversely, smaller complexes do not typically have lifetime issues, but they may have strong binding interactions which are greater than the incident photon energy. Depending on the strength of the binding, multiphoton absorption may be able to access a photodissociation channel, but this process is typically inefficient due to the typically low laser fluences available with our IR sources. Thus both large and small complexes may absorb IR photons, but their photodissociation may be inefficient and below the sensitivity of our apparatus. To deal with these issues other techniques were developed to permit the study of such systems.

To study systems where photodissociation is otherwise inefficient, a couple of strategies can be implemented. For small complexes where the binding of the ligand is directly to the metal and fragmentation is not possible with a single photon, we employ the technique of "tagging".^{73, 255, 256} The idea here is that the binding interaction of a spectator molecule or atom (such as Ne, Ar, H₂ or N₂) is comparable to or less than the excitation photon energy. Moreover, the binding energy of the spectator ligand is expected to decrease in a system with additional ligands. Upon absorption on resonance, the tagged metal ion-ligand complex fragments via the loss of the tagging molecule or atom and a spectrum can be recorded. But the question may be asked, "What are the effects of the spectator ligand on the untagged complex?" Using theory, we can investigate the impact that the spectator ligand has on the untagged complex and ascertain whether it truly behaves as a spectator or participates more strongly in the complex's energetics and significantly affects its structure. As discussed in Chapter 5, we use this technique with the rare gas Ar to study the IR photodissociation of M⁺(acetone), M = Mg, Al, Ca.

A second approach for measuring the spectra of strongly bound systems is to look for spectra associated with complexes that have a large number of ligands. For larger systems, especially multiple ligand complexes, there is often a saturation point for metal-ligand binding, which may correspond to the gas phase coordination number of the metal ion. When the number of ligands exceeds the active binding sites on the metal, then a "second sphere" of ligands results which is bound by only ligand-ligand interactions. This binding is expected to be similar to that of the pure molecular dimer, and in the case of (CO)₂, it is only ~150 cm^{-1.257} As the vibrations typically probed with our current instrument have frequencies that are much higher than this value, the pure ligand interaction may result in efficient photodissociation with a single resonant IR photon, and a spectrum may be recorded.

We have studied many complexes of the form $M^+(CO_2)_n$, and their spectra are typically blueshifted relative to the free molecule, in the region of the CO₂ antisymmetric stretch (2349 cm⁻¹).²⁰⁵, ^{238-242, 254, 258} The blue-shift arises from the electrostatic nature (ion-quadrupole) of the binding, and it was found that the CO₂ binds end-on to the M^+ through an oxygen. In di-ligand complexes, where a transition metal is at the core, the structure was found to be linear; however, Mg^+ forms bent structures with two ligands.²⁴⁰ This effect was discussed in light of the polarization that the first ligand has on the 3s¹ electron of the magnesium cation: to minimize repulsion, the second ligand binds on the same side as the first. In a similar vein, our group has investigated the interaction of metal cations with benzene²⁴⁷⁻²⁴⁹ and acetylene,^{245, 246, 259} studying the nature of their bonding through photodissociation in the region of the C-H stretch (~3000-3400 cm⁻¹, depending on the molecule). As reported in those works, the direction and magnitude of a vibrational shift can help to understand the interplay of covalent and electrostatic interactions in the mechanism of their binding.

Our IR-REPD studies of $M^+(H_2O)_n$ probed the antisymmetric and symmetric OH vibrations of water near 3700 cm⁻¹.^{72, 260} These spectra indicated that the OH vibrations red-shift upon binding to metal. This is the result of charge transfer in the metal-water interaction, weakening the OH bonds and shifting their vibrations to lower values.^{72, 260} Vanadium cation mono-water spectra had resolved rotational structure, by which bond lengths and angles could be deduced.⁷² Furthermore, analysis of the rotational structure yielded a rotational temperature near 35 K for the complexes produced in our instrument. Since water is so fundamental to life and our planet, these studies are important basic research for understanding more complicated metal-water interactions.

Related to the work presented in this dissertation, we recently investigated metal-dinitrogen complexes with IR-REPD.^{243, 244} The nitrogen molecule is isoelectronic with CO, but unlike CO has no IR active stretching vibration, being a homonuclear diatomic. Scanning in the region near 2300 cm⁻¹,²⁶ we found that the N-N stretch is "turned on" upon complexation to the metal ions V⁺ and Nb^{+, 243, 244} We discovered that the N₂ ligand prefers to bind to the metal cation end-on, and the complex's N-N stretch red shifts relative to the bare dinitrogen stretch. Using IR-REPD and theory, we were able to probe the coordination number for these metal-dinitrogen complexes as well as their structures.

IR-REPD spectroscopy has proven itself to be a valuable tool to probe the structures of many metal-ligand systems in the gas phase. In coupling these experiments with calculations, much information about the energetics, structures and bonding of a given system can be determined. Using this technique, we present here our studies of gas phase metal carbonyl complexes in the region of the free CO stretch (2143 cm⁻¹),²⁶ and metal bound to acetone in the region of its free carbonyl stretch (1731 cm⁻¹).²⁵⁴ Chapter 2 outlines the experimental conditions used to study the metal ion-carbonyl complexes. In subsequent chapters, we look into the gas-phase organometallic binding of atomic Au⁺ and Pt⁺ to CO and the binding interactions of Mg⁺, Al⁺ and Ca⁺ with the organic molecule acetone. For the gold carbonyl complexes, clearly "nonclassical" metal carbonyl behavior is observed, with significant blue shifts relative to the free C-O stretching frequency. This phenomenon is discussed with the help of high level calculations in Chapter 3. In the platinum carbonyl complex-es studied, slight blue shifts are observed, and this is examined in light of the synergy associated with

the Dewar-Chatt-Duncanson model in Chapter 4. Due to the intrinsic challenge associated with calculations for the open shell platinum cation, no high level theory is available for those systems. For the main group metal cation-acetone complexes, we examine the spectral shifts near the carbonyl stretching region of acetone (1731 cm⁻¹)²⁵⁴ and interpret them with density functional theory. These complexes show classical, strongly red-shifted metal carbonyl behavior, which is discussed in Chapter 5.

1.4 References

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CHAPTER 2

EXPERIMENTAL

The fundamental characteristics of a given molecular complex can be complicated by solvent interactions, ambient thermal energies and other condensed-phase interactions. Furthermore, metal complex species often possess a net charge or are highly reactive, which may result in the system not surviving ambient atmospheric environments. The capability to generate and isolate a given molecular complex in the gas phase can enhance the ability to interpret its spectrum and therefore its structure, bonding and energetics.¹ Our approach to generating and studying metal-ligand complexes is to couple a laser vaporization source with a mass spectrometer and study them with photodissociation action spectroscopy.²

2.1 The Molecular Beam Apparatus

To generate and characterize metal complex species, a molecular beam apparatus is employed, as shown in Figure 2.1.^{3, 4} This apparatus consists of two differentially pumped vacuum chambers. The first chamber is where complexes are synthesized and supersonically cooled using laser vaporization of a metal rod (discussed below) coupled to a pulsed nozzle. This chamber is pumped using a Varian VHS-10 oil-diffusion vacuum pump (pumping speed ~5300 l/s for He) backed by a Welch 1375 mechanical pump. A Nd:YAG laser is focused on the metal rod to create a plasma. The generated plasma contains cationic (studied here), neutral and anionic species as well as energetic electrons. Because the positive and negative species in the plasma balance, it has no net charge and is a so-called neutral plasma. This metal plasma is entrained in a rapidly expanding pulse of buffer gas, in which ligands of interest are usually seeded. Subsequently, this expansion is skimmed into the analysis chamber. This second chamber incorporates a homemade reflectron time-of-flight mass spectrometer modified to allow photodissociation studies. It is maintained at Figure 2.1 The molecular beam apparatus. It is composed of two differentially pumped units, the source chamber and a modified reflectron time-of-flight mass spectrometer for the study of gas phase metal-ligand complexes.



about 10⁻⁷ torr with a Varian VHS-6 diffusion pump (2400 l/s for He) backed by a Welch 1397 mechanical pump.

2.2 Pulsed Laser Vaporization

To produce complexes containing metal atoms, we use laser vaporization combined with a pulsed nozzle supersonic expansion.^{2, 5} Such a source can effectively produce complexes with nearly any metal, semi-metal, alloy or non-metal that can be formed into rods of 1/8-, 1/4-, or 1/2-inch diameter. In these experiments, the vaporization laser is a pulsed, high power Nd:YAG (Spectra-Physics INDI-30-10) operating at a repetition rate of 10 Hz. Either the second harmonic (532 nm) or third harmonic (355 nm) of the Nd:YAG may be employed, but for all experiments performed here, the third harmonic was used with a pulse energy of 0.5-5 mJ. Each pulse has a near-Gaussian spatial profile with a diameter of ~7 mm and a time duration of 10 nsec. A quartz lens (focal length ~35 cm) is used to focus the pulsed laser beam to approximately 0.5-1 mm on the rod, depending on the diameter of metal rod used. Typically smaller diameter rods require more focused vaporization laser beams. The metal rod of interest is attached to an external stepper motor through homemade reduction gearing which rotates and translates it at a controllable rate to constantly expose fresh metal surface. Inside the source chamber, the rod is mounted in a specially designed holder that aligns its edge with the pulsed nozzle orifice and has an aperture to admit the vaporization laser pulses. In all experiments performed, the so-called cutaway rod holder design was employed, although other holder designs may be used for the study of different types of metal complexes (e.g. multiple metal systems).⁶ Figure 2.2 shows a diagram of the cutaway rod holder design while Figure 2.3 is a photo of the rod mounted in the holder. The high intensity, focused laser beam impinges on the metal rod of interest and causes localized heating. Thereby, the metal is ablated and the ensuing

Figure 2.2 The cutaway rodholder. This design produces copious quantities of $M^+(ligand)_n$ and $M^+(ligand)_nAr$ complexes.

Vaporization Laser



Figure 2.3 Photo of the rod and rodholder in the source chamber. An aluminum rod is mounted in the specially-designed cutaway rod holder. The skimmer is visible on the left side of the chamber.



plasma can reach very high temperatures (several thousand Kelvin). As mentioned, the neutral plasma becomes entrained in the pulsed buffer gas (usually Ar or He) seeded with atomic and molecular ligands of interest. A Series 9 General Valve controlled with the Iota One controller pulses this buffer gas mix into the chamber. The valve orifice diameter is 0.5 mm and the gas is typically admitted at pressures ranging from 4-18 atmospheres. The buffer gas collisions thermalize the hot plasma to a temperature near 300 K. Subsequently, the entrained pulse of gas expands in the vacuum chamber supersonically, rapidly cooling the species in the expansion. Because of the large gas pulses, large pumping capacities are requisite for this chamber. Timing and synchronization of the laser and gas pulses are achieved via external digital delay generators (Stanford Research Systems DG535). By controlling the delay between the laser and nozzle firing, the complex distribution can be optimized for the desired study.

Because all of the complexes studied here are single metal atom species, the cutaway rod holder design serves as the best choice. It allows immediate expansion after the buffer gas flows past the laser generated plasma, which typically produces atomic metal ion complex species of the form M⁺(ligand)_n. This rapid expansion minimizes collisions between complexes and allows very weakly bound and multi-ligand species to be studied. Hence, the systems resulting from the super-sonic expansion are frozen into their configurations and geometries.

Ligands of interest may be introduced in various ways. Sometimes the buffer gas itself can serve as the ligand of interest; hence, it can serve both as a thermalizing medium and the source for the ligands binding to the metal cation. Other ligands that exist as gaseous molecules (e.g. CO or CO₂) may be mixed with the inert buffer gas at a partial pressure. Ligands which derive from liquidphase molecules, such as acetone, have a finite vapor pressure and can be introduced into a specially designed small chamber attached to a manifold. This mixing chamber is filled with a Kimwipe® and several drops of acetone are added. The chamber is then sealed and the buffer gas is allowed to flow through the Kimwipe®, picking up the ligand of interest. This chamber can be cooled in a bath or heated resistively to control the vapor pressure, but in practice, ambient temperature and time allow for an equilibrium to be established which facilitates targeted complex growth. Ligands derived from solids were not examined in these studies, but resistive heating can enhance their vapor pressure for entrainment. In most experiments one or two drops of water is added to the manifold lines. It has been empirically determined that water facilitates the growth of metal cation complexes, particularly weakly bound species. As discussed elsewhere, it is believed that water facilitates their growth by scavenging electrons in the plasma.³

2.3 Complex Selection and Detection

The supersonic expansion is skimmed with a 3 mm orifice cone (Beam Dynamics, Inc) located ~10 cm downstream that serves as the portal to the second chamber. This skimmer samples a very small portion of the supersonic expansion and produces a collimated molecular beam. At this point, the beam still contains a mixture of electrons, ions and neutrals, but in this second chamber, only cations are selected for study. Because only a fraction of the original gas pulse is skimmed, this chamber does not have the pumping requirements of the source chamber, so a smaller vacuum system is used. But it is essential that this chamber is maintained at high vacuum, ~10⁻⁷ torr. In this pressure region, the mean free path of the molecules (several meters) is such that no collisions occur while the complexes travel through the rest of the apparatus, preserving them.

For mass analysis, a Wiley-McLaren reflectron time-of-flight mass spectrometer is used to study the positively charged species.⁷ A pair of pulsed acceleration plates, which form the starting

point for the mass analyzer, selects the cations. Because the molecular beam has a finite volume, this design minimizes the spatial effects that limit mass resolution. Moreover, this mass spectrometer extracts ions perpendicularly from their initial flight path, effectively minimizing any initial velocity in the direction of extraction. The design consists of a repeller plate and draw-out grid (DOG), both biased by switched voltages, and a dc-ground plate. The biasing potentials applied to the repeller and DOG are typically 1000 V and 900 V, respectively. The electric field serves to give the ions the initial energy push necessary to fly through the mass spectrometer. Because the plates are biased with a positive polarity, cations in the molecular beam are extracted while anions are rejected and neutrals pass through unaffected. A horizontal deflection plate is also implemented on the axis of the beam to compensate for the transverse velocity inherent in the direction of the molecular beam. This plate may have an applied potential that is varied, typically 0-120 V. Once the cations are extracted, an einzel lens serves to focus the ion packets, affecting them in a way similar to an optical lens' ability to focus light. Like most of the parameters in the mass spectrometer, the biasing voltage of the einzel lens may be varied (0-1000 V) to yield efficient complex detection.

Since the ions all start out with the same energy provided by the electric field from the repeller/DOG/ground plate, they will separate according to their mass-to-charge ratio. This relationship may be expressed as

$$E = qV = \frac{1}{2}m_o v^2 = \frac{1}{2}m_o \left(\frac{d}{t-t_o}\right)$$
 Equation 2.1

where q is the charge of the ion, V is the voltage applied, m is the ion's mass, v is its velocity, d is the flight length and t is the time in transit. Because all species studied here are monocations, the time of flight of each ion is directly related to its mass. To assign masses, a channel of known mass is first chosen, relying on the isotope pattern or other known features of the spectrum. Then, the remaining masses may be assigned according to the expression

$$\frac{m_i}{t_i^2} = \frac{m_o}{t_o^2}$$
 Equation 2.2

which follows from Equation 2.1.

At the end of the first flight tube, a stack of ten parallel plates forms the reflectron field. The plates have applied dc voltages that serve to slow down and redirect the ion packet to a second flight tube. The typical voltage bias is 1350 V at the back of the reflectron plates to ground at the entrance of the reflectron, divided evenly over the ten plates. The mass spectrometer has enhanced resolution from the reflectron's refocusing of the ion packet. Also, the reflectron has been modified to allow photodissociation studies, as discussed below.

Ions are detected, whether probed with laser spectroscopy or not, with an electron multiplier tube detector (Hamamatsu R595) at the end of the second flight tube. This detector provides an amplification of about 10⁷, and the signal generated is amplified by a fast, variable preamplifier (Stanford Research Systems SR445A). This device typically is set to amplify the signal by a factor of 5X. A Lecroy (WaveRunner LT-342) digital storage oscilloscope (DSO) then collects the signal. Data is transferred from the DSO to a PC via a standard IEEE-488.2 protocol interface where it can be analyzed. Interfacing and control of the PC, DSO and photodissociation laser is accomplished with custom-written software coded in MS Visual Basic 6, SP5. A typical mass spectrum collected with the instrument is shown in Figure 2.4.

In order to select the particular mass channel of a single metal complex, a pair of plates are mounted in the flight tube on either side of the ion's flight path. These plates are held at a constant **Figure 2.4** Mass spectrum of $Pt^+(CO)_n$. The small mass progression not labelled is $Pt^+(CO)_n(H2O)$. This represents a typical mass spectrum produced by the laser vaporization/mass spectrometer molecular beam machine. Note that the platinum cation is off-scale.



potential of 250-400 V before and after the ion of interest passes to deflect these other ions into the wall of the flight tube. To allow the desired ion packet through, the plates are quickly switched to ground for a short duration using a custom designed switching power supply (Directed Energy, Ft. Collins, CO). This is shown schematically in Figure 2.5. This feature of the mass spectrometer provides the ability to spectroscopically investigate complexes of *known* mass. With this arrangement, the first flight tube serves to select an ion complex as a parent mass channel, photodissociation takes place in the reflectron region and the second flight tube allows mass analysis of the parent and any fragments.

For spectroscopic studies, the reflectron has been modified for photodissociation studies of a given complex with the addition of a pair of windows.^{8,9} These two inch windows must have high transmission with minimal losses throughout the wavelength region scanned. In practice, we find that windows of ZnSe with an anti-reflection coating work well over the tuning range of the laser down to the far-IR wavelengths. They are placed such that high peak-power pulsed laser light may intersect the beam at the turning point of the ion packet in the reflectron. Control of the intersection position is achieved by two externally mounted gold mirrors. Additionally, an external gold concave mirror can be used to reflect and focus the laser beam back through the reflectron for increased fluence in the interaction zone.

Spectra may be collected either at fixed photodissociation wavelength or by tuning the infrared laser. When collecting photodissociation spectra at fixed wavelengths, on resonance, a difference mass spectrum is generated. Here, a mass spectrum is collected with the resonant photodissociation laser "off" (no fragmentation channels) and subtracted from a subsequent mass spectrum collected with the laser "on" (fragmentation and parent channels present). The result is a mass specFigure 2.5 The mass selection process. In the upper figure, ions pass unhindered. A voltage causes deflection of the ions as shown in the middle figure. The lower figure shows how ions of interest are selected by the rapidly switching the applied voltage ground.



trum that shows fragment channels as positive peaks and the parent channel as an ion depletion peak. An example of such a difference mass spectrum generated from resonant photodissociation laser on/laser off spectra is shown in Figure 2.6. Likewise, spectra can be obtained by tuning the infrared light source. When the laser light comes on resonance, fragmentation channels may grow in. Hence, monitoring a fragment channel or channels as a function of infrared wavelength results in an infrared action spectrum. In either the fixed- or tuned-frequency case the resonant infrared photon must be of sufficient energy to cause efficient fragmentation of the ion studied for a signal to be detected. In cases where the infrared photon energy is of insufficient energy to cause fragmentation, no signals may be observed. To study the spectroscopy of such systems, spectator ligands may be attached (often rare gases such as Ar) to the nascent M⁺(ligand)_a ions employing a technique known as "tagging".^{4, 10-12} Binding energies of these spectator ligands to the complex are often much less than the infrared photon energy, and so fragmentation may become efficient in the tagged species. Thus, tagging opens up the possibility to study metal ion complexes which would otherwise be inaccessible to photodissociation studies. In all cases, this method of obtaining action spectra is highly dependent on tunable infrared light sources.

2.4 Tunable Infrared Light Source

Because of the low densities of metal-containing complexes produced and the relatively small volume of the molecular beam, traditional infrared absorption experiments are not practical. Instead, we rely on infrared lasers to measure action spectroscopy via photodissociation in a chosen metal ion complex. Hence we require tunable sources of infrared radiation of sufficient power to initiate fragmentation. We can then monitor the fragment yield as a function of laser wavelength. Until relatively recently such infrared sources were unavailable, but laser systems have become avail Figure 2.6 The method of generating a difference mass spectrum for $Au^+(CO)_6$. In the top trace, a mass spectrum is recorded with photodissociation laser "on". Subsequently, a mass spectrum is recorded with photodissociation laser "off" as in the middle trace. Subtraction results in a difference mass spectrum, shown in the lower trace.



able in the last decade which permit studies spanning the IR region 2000-4500 cm⁻¹.^{4, 13-15, 15-20} Furthermore, new developments in crystal technology and availability permit studies below 2000 cm⁻¹.²¹⁻²⁴

We employ a LaserVision optical parametric oscillator/optical parametric amplifier (OPO/ OPA) system pumped by the fundamental of a high power, injection-seeded Nd:YAG laser (Continuum 9010) running at 10 Hz. A diagram of the optical train for the OPO/OPA is given in Figure 2.7. The typical pump energy from the Nd:YAG laser is 600 mJ/pulse which is split into two beams with an energy ratio of ~2:1. Approximately 200 mJ/pulse of 1064 nm laser light is converted to the second harmonic (532 nm) and used to pump the OPO stage. The balance of the pump energy is mixed with the output from the OPO in the OPA stage for the generation of mid-IR wavelengths (~2.2-5 μ m, 2000-4500 cm⁻¹).

The OPO stage consists of two potassium titanium oxide phosphate (KTiOPO₄, known as KTP) crystals, with dimensions of approximately 7x7x15 mm. They are angle tuned using servomotors to achieve phase matching. The paired crystals counter-rotate to each other to facilitate the parametric process and compensate for any translation effects of the beam in the medium. The cavity includes a grating to limit the bandwidth of the system to below a wavenumber and an output coupler. When phase-matching conditions are met, this oscillator generates two beams, a signal and idler, in a process known as downconversion. These beams are related according to the relation,

$$\omega_{pump} = \omega_{signal} + \omega_{idler} \qquad \qquad \text{Equation 2.3}$$

where the following convention is used: $\omega_{signal} > \omega_{idler}$. Here, ω is the energy of the radiation in reciprocal centimeters. Signal wavelengths are from 710-845 nm and idler wavelengths span 1350-2000 nm. The signal is not used further in the OPO/OPA, but can be monitored as a diag-

nostic. The idler beam is sent to the OPA stage for difference frequency mixing to generate mid-IR wavelengths.

The OPA state consists of four potassium titanyl arsenate (KTiOAsO₄, or KTA) crystals (7x7x15 mm). As in the OPO, the OPA crystals are angle tuned to achieve phase matching conditions. These crystals are in two matched pairs, with each pair counter-rotating to minimize beam walk. In this stage, difference frequency mixing (DFM) is used to generate tunable light in the mid-IR region (2000–4500 cm⁻¹). This process generates a new beam by taking the difference of two incident beams according to

$$\omega_{\text{mid}-IR} = \omega_{1064\,\text{nm}} - \omega_{OPO\,Idler}, \qquad \text{Equation 2.4}$$

and relies on nonlinear crystals that are optically transparent to all three wavelengths. Typical output energies in the mid-IR region are 0.5-15 mJ/pulse, depending on wavelength with linewidths less than a wavenumber.

While many molecules and ligands have infrared stretching vibrations above 2000 cm⁻¹, the bulk of traditional infrared fingerprint vibrations fall below the tuning curve of the stand-alone OPO/OPA. For example, many carbonyl-complex stretches fall in the region from 1600-1800 cm⁻¹, many ring-based modes occur below 1500 cm⁻¹ and many bending modes occur below 1000 cm⁻¹. Until recently, the low frequency IR spectrum was accessible only by free-electron lasers (FELs). FELs are expensive to build and maintain and require significant space. Moreover, due to the intrinsic nature of the radiation generated by an FEL, multiple photon absorption often leads to power broadening of spectra.

However, new and exciting developments in crystal technology have permitted the extension of tunable infrared light below 2000 cm⁻¹ to \sim 700 cm⁻¹ for use in spectroscopic studies.^{25, 26} These

crystals, coupled with a standard mid-IR OPO/OPA, have paved the way for experiments which fit on the laboratory bench top and yield linewidths comparable to that of the OPO/OPA laser itself. A silver gallium selenide (AgGaSe₂, with dimensions of 7x7x25 mm) crystal added outside of the OPA mixes its signal and idler outputs. From the difference of these beams, a far-IR output beam is generated in a process similar to that in the OPA stage. The crystal is mounted on a rotating stage and angle tuned by a servomotor. Because of the long wavelengths produced beam walk is at a minimum, even in the single crystal. Typical output energies are 50-500 µJ of tunable far-IR energy, depending on wavelength, with linewidths comparable to the OPO/OPA itself. Figure 2.7 depicts the AgGaSe₂ as a add-on to the OPO/OPA for far-IR generation. The output is filtered through a germanium window, which transmits only far-IR light to the experiment. With this crystal, infrared photodissociation spectroscopy is opened to many new possibilities for probing chemically interesting metal complexes in a bench top laboratory setting.

Figure 2.7 Diagram of the mid-IR laser. It is an optical parametric oscillator/optical parametric amplifier(OPO/OPA) that uses difference frequency mixing (DFM) for generation of mid-IR wavelengths (2000 - 4500 cm⁻¹).


Figure 2.8 Diagram of the IR OPO/OPA with the external AgGaSe₂ crystal for the DFM generation of far-IR wavelengths. This crystal effectively extends the tuning range of our instrument down to \sim 700 cm⁻¹.



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CHAPTER 3

GAS PHASE INFRARED PHOTODISSOCIATION SPECTROSCOPY AND THEORY OF

Au⁺(CO)_n COMPLEXES¹

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3.1 Abstract

 $Au^+(CO)_n$ complexes are produced in the gas phase via pulsed laser vaporization, expanded in a supersonic jet and detected with a reflectron time-of-flight mass spectrometer. Complexes up to n = 12 are observed, with channels corresponding to the n = 2 and n = 4 showing enhanced intensity. To investigate coordination and structure, individual complexes are mass-selected and probed with infrared photodissociation spectroscopy. Spectra in the carbonyl stretching region are measured for the n = 3-7 species, but no photodissociation is observed for n = 1, 2 due to the strong metal cation-ligand binding. The carbonyl stretch in these systems is blue shifted 60-70 cm⁻¹ with respect to the free CO vibration (2143 cm⁻¹), providing evidence that these gas phase complexes are so-called nonclassical metal carbonyls. Theory at the MP2 and CCSD(T) levels provides structures for these complexes and predicted spectra to compare to the experiment. Excellent agreement is obtained between experiment and theory, establishing that the n = 2 complex is linear, the n = 3 complex is trigonal planar and the n = 4 complex is tetrahedral.

3.2 Introduction

Transition metal-carbonyl chemistry has a long and rich history that spans well over a century. Many examples of transition metal-carbonyl complexes have been synthesized and characterized throughout inorganic and organometallic chemistry, and some of these systems are used for homogeneous catalysis processes.^{1,2} At a more fundamental level, TM-carbonyls are important models for complex systems such as chemisorption on metal surfaces³ or the binding of small molecules at the active sites of metallo-proteins. Infrared and Raman vibrational spectroscopy of metal carbonyls provides a convenient probe of their chemical environment.⁴ Gas phase metal carbonyl ions have been studied extensively in mass spectrometry.⁵⁻⁷ The structures and bonding of these ions have been investigated with theory.⁶⁻²⁰ The reactions of carbonyl ions have been well characterized, and bond energies have been determined,²¹⁻²⁹ but there is much less data on their spectroscopy. However, experiments have employed photoelectron spectroscopy to obtain information about the corresponding neutral ground state's vibrational levels.³⁰⁻³⁴ Infrared spectroscopy has been used to measure vibrational spectroscopy for a variety of metal atom and metal cluster carbonyl ions in rare gas matrices.7, 35-38 Moreover, infrared photodissociation measurements have been described for metal cluster carbonyl cations using free electron lasers.³⁹⁻⁴⁴ In the present study, we employ similar methods to investigate the unusual carbonyl complexes of gold cations with benchtop infrared laser systems.

The bonding in transition metal carbonyl compounds is often understood in light of the classic Dewar-Chatt-Duncanson complexation model.^{1, 6, 7, 45, 46} In this picture of classical metal-carbonyl bonding, two general types of interactions contribute to the formation of the metal-CO bond. The CO contributes electron density from its HOMO on-axis, forming the dative σ bond.

But π back-bonding occurs by donation of electron density from the partially filled d-shells of the metal into the LUMO of CO. In so-called classical metal-carbonyls then, the C-O stretching frequency is lowered and its bond lengthened because of the loss of bonding electron density and the gain of antibonding electron density in the LUMO on CO. It is interesting to note that the majority of transition metal carbonyl complexes show this classical behavior. In contrast to this, examples are known of non-classical carbonyl bonding, which usually occurs for systems with filled d electron shells that are not able to donate or accept charge efficiently.^{17, 18, 47-50} The noble metal *atomic* ions are known to form such non-classical carbonyls in the condensed phase.⁴⁷⁻⁵⁰ Although noble metal *cluster* complexes with carbonyls have been studied with gas phase infrared spectroscopy,⁴¹⁻⁴³ there is no previous gas-phase spectroscopy for the atomic M⁺(CO)_n species of these metals.

Haruta's discovery⁵¹⁻⁵⁵ of the ability of gold nanoparticles on a metal oxide support to oxidize CO at low-temperature has stimulated many investigations into the properties of gold clusters supported on metal oxide surfaces.⁵⁶⁻⁶¹ In all of these studies, a common theme has been the cooperative effects of the metal cluster and its support. Related to this, both gas-phase experiments and theory have documented the unusual catalytic activity found for small gold clusters and how this activity varies with cluster size, charge state and the nature of the support.⁶²⁻⁷⁶ The intrinsic reactivity of the pure metal cluster system or its support without the metal are difficult to distinguish with experiments or theory. However, gas phase measurements of isolated metal systems may be able to provide needed insight in this area.

Condensed-phase vibrational spectra of cationic gold carbonyls show a marked increase in the stretching frequency of metal-bound CO compared to free gas phase CO (fundamental = 2143 cm⁻¹), depending on the metal, earning these compounds the designation as nonclassical carbonyls,

as noted above.^{6-20, 47-50} In the case of gold-carbonyl systems in condensed media, the blue shifts measured were significant.⁵⁰ Numerous theoretical studies have discussed the origins of this vibrational blue shift, which appears to be unique to only a few metals, including the noble metals.⁶⁷⁻²⁰ Several groups have collected infrared spectra for cationic, neutral and anionic gold-carbonyl clusters (as well as many other metal-carbonyl systems) frozen in rare-gas matrices.^{35, 37, 38} Infrared spectra were recorded for CO bound to cationic gold clusters, Au_n⁺ (n=3-20) in the gas-phase by Meijer and co-workers.^{41, 42} Castleman and co-workers studied CO interacting with cationic gold oxides.⁷¹ And recently, microwave spectra have been obtained for gas-phase OCAuX (X = F, Cl, Br and I).^{77, 78}

Using infrared photodissociation spectroscopy to investigate bonding and structure, our group has studied a number of transition metal-ligand systems with interest in organometallic chemistry. In particular we have measured infrared spectra for several different metal cations with multiple CO_2 ligands.^{79, 80} We have studied acetylene bound to Ni⁺ to determine the coordination number as well as the structures of these small complexes.⁸¹ Furthermore, we have measured infrared spectra for N₂ complexes (isoelectronic with CO) with V⁺ and Nb⁺.^{82, 83} And we have observed shifts of the carbonyl stretch on acetone when binding to cations such as Mg⁺, Al⁺ and Ca⁺.⁸⁴ Using these same methods, we investigate the nonclassical species Au⁺(CO)_n (n = 3-7) in the gas-phase and interpret the spectra with ab initio calculations to understand the structure and bonding in these systems.

3.3 Experimental

Gold-carbonyl cation complexes are produced by 355 nm pulsed laser vaporization (Spectra-Physics Indi 30-10) of a ¹/₈ inch gold rod sample mounted in a rotating rod, pulsed nozzle source.⁸⁰ The rod holder used in these experiments is the so-called cutaway design.⁸⁰ The expansion gas is a mixture of 2% CO in Ar, by partial pressure. Depending on source conditions, various $Au^+(CO)_n$ complex size distributions are produced. These complexes are detected and mass-selected with a reflectron time-of-flight mass spectrometer, as described previously.⁸⁰ Tunable infrared radiation is produced with a specially designed infrared optical parametric oscillator/amplifier (OPO/OPA) system (LaserVision) pumped with a Nd:YAG laser (Continuum 9010). The linewidth of the OPO/ OPA is about 0.3 cm⁻¹, and its pulse energy is 1-2 mJ in the wavelength region scanned here. Excitation of the mass-selected ions takes place in the turning region of the reflectron, and fragment mass analysis occurs in the flight tube section after this. Monitoring fragments as a function of infrared frequency generates an infrared spectrum in the carbonyl stretch region (2140 to 2270 cm⁻¹). To establish breakdown patterns of larger species (and thus elucidate gas-phase coordination), the laser is set to the resonance frequency of the selected complex. Then mass spectra are recorded with the photodissociation laser "on" followed by a recording with the laser "off". The difference of these spectra reveals the resonant fragmentation patterns of a selected metal complex. These fragmentation patterns can suggest gas phase cation-ligand coordination numbers, as terminal fragment ions can lose outer ligands to yield stable geometries that result from inner-sphere ligands binding directly to the metal..

All calculations were done by our collaborators, Gordon and coworkers, using the GAMESS^{85, 86} program suite with the MacMolPlt⁸⁷ program being used to visualize the molecules. Calculations were performed employing the cc-pVDZ85⁸⁸ (abbreviated here as ccd), cc-pVTZ85⁸⁸ (cct) or cc-pVQZ85⁸⁸ (ccq) basis sets on carbon and oxygen atoms. The gold atom was treated with 19 explicit electrons using the SBKJC⁸⁹ effective core potential (ECP) with scalar relativistic corrections augmented with a 3f/2g set of polarization functions with f function exponents of 2.00, 0.84 and 0.31, and g function exponents of 1.90 and 0.69, and one set of s and p diffuse functions with

exponents of 0.01. Spherical gaussian functions were used. Second order perturbation theory $(MP2)^{90.93}$ or coupled cluster $(CCSD(T))^{94}$ levels of theory were used. The molecules were considered in their full point group symmetries. Molecules were tightly optimized⁹⁵⁻⁹⁷ with the largest component of the gradient required to be less than $1x10^{-5}$ Hartree/bohr, using MP2 analytical gradients and CCSD(T) numerical gradients.

A normal mode analysis⁹⁸ was performed using MP2 seminumerical Hessians and fully numerical CCSD(T) Hessians. Hessians were calculated using double differencing of the energy with 0.01 Bohr displacements from the equilibrium geometry in both positive and negative directions. Anharmonic frequency calculations were performed using the vibrational self consistent field (VSCF) method.⁹⁹ A grid of 16 points is created for each normal mode by making 8 displacements from the equilibrium geometry in both the positive and negative directions. In order to account for mode-mode coupling, simultaneous displacements from the equilibrium geometry were made along two normal mode displacement vectors; this generates a two-dimensional grid of 16x16 points. Electronic structure calculations were performed at each of these points. Anharmonic coupled vibrational frequencies were calculated using a second order perturbation theory correction for the vibrational self consistent field calculation.

3.4 Results and Discussion

The laser vaporization source efficiently generates varying sizes of gold-carbonyl cations as well as other minor species. Figure 3.1 shows a mass spectrum of $Au^+(CO)_n$, for n up to 12, where the gold cation peak is off-scale. Depending on source conditions, complex sizes up to n = 24 can be grown, but for this study, the focus is on those with n < 7. The small peaks interspersed between the $Au^+(CO)_n$ peak are $Au^+(H_2O)(CO)_n$. The salient feature of the mass spectrum is the significantly

Figure 3.1 Mass Spectrum of $Au^+(CO)_n$ showing optimized conditions for small values of n up to 12. The Au^+ cation is off-scale, while the small series not labeled is $Au^+(H_2O)(CO)_n$.





enhanced intensity for the n = 2 mass channel, which occurs independent of source or mass spectrometer focusing conditions. This enhanced intensity suggests that the n = 2 complex is more stable than other stoichiometries, as would be the case if this is the preferred coordination number for gas-phase gold cation.

To investigate gold cation coordination we measured the fragmentation behavior of these complexes with resonant photodissociation mass spectra. For these measurements, a particular mass channel was selected and the IR laser scanned in the region where the C-O stretching resonances are expected until a photodissociation signal was apparent. The mass spectrum was then recorded with the photodissociation laser "off" and then subtracted from that recorded with the laser "on". The resulting difference spectrum shows the breakdown of a parent channel into one or more fragment channels. In the case of gold-carbonyl cation, no fragmentation signal could be found for the n= 1 and 2 complexes. These complexes should have IR-active vibrations in this region, and strong resonances are predicted by theory (see below). However, the absence of observed photodissociation points to a cation-carbonyl binding that is too strong to be broken by infrared excitation at this energy for the n = 1 and 2 complexes. Hence, we can conclude that the Au⁺(CO) and (CO)Au⁺(CO) binding energies are in excess of the infrared photon energy that would excite the C-O stretches in these complexes ($\sim 2200 \text{ cm}^{-1}$ or 6.3 kcal/mol). The larger complexes with more CO ligands do yield an observable photodissociation signal, as shown in Figure 3.2 for the n = 3-6complexes. These systems lose a single CO ligand upon resonant excitation with infrared radiation. The photodissociation laser pulse energy used is low, about 1 mJ in an unfocused 3 mm diameter spot, and the fragmentation channels vary with laser pulse energy consistent with a single photon process.

Figure 3.2 Difference mass spectra of $Au^+(CO)_n$ (n = 3-6). Each parent channel fragments by loss of CO. No photodissociation is observed for the n = 1 and 2 complexes.



We can therefore conclude that the CO binding energy for the n = 3-6 complexes is less than the IR photon energy (~2200 cm⁻¹). The only previous experimental information on these bond energies comes from the work of Schwarz and co-workers.²⁹ They found a bond energy for Au⁺(CO) of 1.95eV (45.0 kcal/mol), consistent with the lower limit obtained here for this ion

To measure vibrational spectra for these complexes, we measure the wavelength dependence of their fragmentation yields. Since the n = 1 and 2 complexes do not photodissociate in our experiment, we cannot study these systems in any way. The usual method for investigating systems where the metal-ligand interaction is greater than the photon energy is rare-gas "tagging".^{79-81, 84, 100, 101} In tagging, a more weakly bound rare-gas atom is added to the complex to enhance the photodissociation yield. We were able to tag both Au⁺(CO) and Au⁺(CO)₂ with Ar, producing small amounts of the desired tagged complex ions. However no fragmentation was observed with these tagged complexes. The binding energy of Ar to Au⁺ in the diatomic was calculated by Pyykko to be ~2600 cm-1.¹⁰² In light of this strong Au⁺-Ar interaction, it is understandable that photodissociation of Au⁺(CO)-Ar or Au⁺(CO)₂-Ar may not be efficient near 2200 cm⁻¹. A more weakly bound spectator ligand should make it possible to observe photofragmentation. But in several tries, we were unable to successfully tag any Au⁺(CO)_n complexes.

The n = 3-6 complexes do fragment near 2200 cm⁻¹, and the measured resonance-enhanced infrared photodissociation spectra for $Au^+(CO)_n$, n = 3-6 complexes are presented in Figure 3.3. In this figure, the value of the free CO stretch is indicated with a red line and the calculated C-O stretch frequencies for n = 3 and 4 are marked with blue lines. Of particular note is that all of these measured spectra exhibit single peaks that are significantly blue-shifted from that of the free C-O

Figure 3.3 Infrared photodissociation spectra of $Au^+(CO)_n$ (n = 3-6). The dashed red line indicates the position of the free C-O stretch (2143 cm⁻¹), while the blue solid lines for n = 3 and 4 indicate the calculated frequencies. No photodissociation is observed for n = 1 and 2.



stretch in carbon monoxide (2143 cm⁻¹).¹⁰³ The solitary peak in the C-O stretching region suggests that these complexes have high symmetry, with equivalent CO ligands. Otherwise, more than one infrared band would be detected. We can then suggest that the n = 3 complex should be trigonal planar, and that the n = 4 complex should be square planar or tetrahedral. The n = 3 complex has its band at 2215 cm⁻¹, which is shifted 72 cm⁻¹ to the blue from the free-CO stretch, and this is the largest blue shift observed here. The n = 4, 5 and 6 complexes have their bands at almost the same positions of 2205, 2204 and 2203 cm⁻¹, respectively. These represent respective shifts of 62, 61 and 60 cm⁻¹. Blue shifted CO vibrations have also been reported previously for condensed phase Au⁺(CO)_n complexes and for complexes isolated in rare gas matrices. In condensed phase studies, the documented blue shifts are 52 and 68 cm⁻¹ for the n = 1 and 2 complexes, respectively. While our spectra begin with the n = 3 complex and so a direct comparison cannot be made, the qualitative trend of blue-shifted CO stretches is apparent. In matrix isolation experiments, shifts of 60 and 50 cm⁻¹ whifts, the agreement between our recorded spectra and reported matrix shifts is rather good.

We also collected a noisy spectrum for the n = 7 complex that is not shown here. In previous studies of metal ion-CO₂ complexes, we have seen an "unshifted" vibrational band signaling the presence of such external ligands.^{79, 80} However, the n = 7 complex only has one blue shifted band at 2201 cm⁻¹, which falls at essentially the same position as the band in the n = 6 spectrum. In the spectrum for the n = 7 complex, there is no band near the position of the free C-O stretch (2143 cm⁻¹) that would indicate an external CO binding. Since CO has a small dipole moment (0.11 D), the IR intensity of such a band is expected to be low, and it is possible we would miss it because of the small signal levels present in this spectrum. We also did not see unshifted vibrations in our previous studies of metal ion- N_2 complexes. Again, this is because the N_2 ligands not directly attached to the metal ion have virtually no IR intensity.

To further investigate the origins of these blue-shifted spectra and to determine the structures of the complexes that might be consistent with these shifts, our collaborators performed calculations at various levels of theory. The calculations were performed using the same basis set for Au⁺ in all cases, while the C and O basis set was varied from ccd to cct to ccq. CCSD(T) optimized molecular geometries employing the ccd basis set are given in Figure 3.4. As shown in the figure, the optimized structures for both the n = 1 and 2 complexes are linear. The n = 3 complex has a trigonal planar structure, and the n = 4 complex is tetrahedral. In each complex, the C-O bond distance is slightly longer than it is for the CO diatomic ($r_e = 1.128$ Å).¹⁰³ The Au⁺-C bond distance is roughly 2 Å, increasing from the shortest value of 1.982 Å for the n = 1 complex up to the longest value of 2.162 Å for the n = 4 complex.

Table 3.1 presents the calculated differential binding energies for the $Au^+(CO)_n$ (n = 1-4) complexes. According to these data, Au^+ has a high affinity for binding the first and second CO molecules, with binding energies in the neighborhood of 50 kcal/mol. The n = 2 complex has slightly higher binding energy for its outer CO than the n = 1 complex. This kind of increase in bond energy upon addition of a second carbonyl ligand has been reported and discussed previously by Armentrout and co-workers.^{21-24, 104-106} A significant decrease in the binding energy occurs here for the n = 3 and 4 complexes, whose outermost ligands are computed to be bound by ~10 kcal/mol. The highest differential binding energy, which occurs for the second CO ligand, and the dramatic decrease in binding energy after this, suggests that the preferred coordination number for Au⁺ in the gas-phase complexes is two CO ligands, consistent with out experimental findings discussed

Figure 3.4 Optimized geometries at CCSD(T) level of theory with the ccd basis set on C and O atoms. The accompanying table indicates complex symmetries and computed Au⁺-C and C-O bond lengths.



Complex	Point Group	Au ⁺ -C bond length (Å)	C-O bond length (Å)
Au ⁺ (CO)	C_{4v}	1.982	1.133
$Au^+(CO)_2$	D_{4b}	2.014	1.132
$Au^+(CO)_3$	D_{3b}	2.102	1.135
$Au^{+}(CO)_{4}$	T_{d}	2.162	1.136

differential binding energies (kcal/mol)						
molecule	ccd/MP2	cct/MP2	ccq/MP2	ccd/CCSD(T)	cct/CCSD(T)	
Au ⁺ (CO)	51.37	49.82	51.19	45.89	43.92	
$\mathrm{Au}^{+}(\mathrm{CO})_{2}$	58.50	56.19	56.17	51.93	49.6	
Au ⁺ (CO) ₃	12.52	10.73		8.76		
$\mathrm{Au}^{+}(\mathrm{CO})_{4}$	13.27	11.80		9.20		

TABLE 3.1: Differential binding energies of $Au^+(CO)_n$, n = 1-4, in kcal/mol.^a

^a Calculations were done at MP2 or CCSD(T) levels of theory using ccd, cct, or ccq basis sets on C and O atoms.

above. This same value for the coordination number of gold cations has been suggested in previous work on condensed phase complexes, and it has been discussed in terms of an s-d(σ) hybridization model.^{9, 10, 12, 14} Such hybridization minimizes the σ repulsion between the filled ligand orbitals and those on the metal, thus enhancing the strong electrostatic component in the binding for the first and second ligands. Back bonding into the π * orbital on CO is also enhanced by this hybridization configuration. However, addition of a third or fourth CO ligand makes the s-d hybridization much less effective, and there is a dramatic drop in the binding energy, as seen here.

The calculated binding energies for these complexes are in qualitative agreement with our experimental data. Experimentally, we find that the binding energy of the outermost CO ligands in the n = 1 and 2 complexes is greater than the ~2200 cm⁻¹ photon energy, which places a lower limit on this binding at 6.3 kcal/mol. The computed values in the 40-50 kcal/mol range at various levels of theory are all consistent with this lower limit, but much higher in value. For the n = 1 complex, our present computed value is in good agreement with the previous experimental result of Schwarz (1.95 eV or 45.0 kcal/mol)²⁰ and in good agreement with the previously calculated value reported by Dargel et al. (2.08 eV or 48.0 kcal/mol)⁸ at the CCSD(T) level of theory. Our theory is also consistent with our experiment in the suggestion that the binding energy drops substantially after the n = 2 for the n = 3 and 4 complexes. However, the calculated values for the binding energies vary by 8-10 kcal/mol, depending on the level of theory. And quantitatively, the computed values are higher than our experimental values. Because we observe efficient photodissociation for the n = 3-6 complexes near 2200 cm⁻¹, we can place a firm upper limit on the outermost CO binding energy of 6.3 kcal/mol.

To improve the computed thermochemistry, the CCSD(T)/cct differential binding energies can be estimated by assuming the improvements due to the use of larger basis sets (e.g., ccd vs. cct) and improvements due to the use of higher levels of theory (e.g., CCSD(T) vs. MP2) are approximately independent of each other. This assumption is fundamental in the popular GN methods of Pople and co-workers.^{107, 108} Using the values in Table 3.1, this approach reduces the n = 3 and n =4 differential binding energies to about 5 and 5.2 kcal/mol, respectively. These values are well within the experimental range. Further improvement to the ccq basis set is expected to have a small effect in the same direction. So, the experiment and theory here both support the dramatic drop in the ligand binding energy for the third and fourth CO, as suggested by the s-d hybridization model. Table 3.2 reports the vibrational frequencies observed in the experiment as well as those computed at the different levels of theory for the various $Au^+(CO)_n$ complexes. The accuracy of the calculated MP2 vibrational frequencies for CO improves somewhat by improving the basis set from ccd to ccq, with the largest improvement obtained by shifting from ccd to cct. The accuracy of the calculations improves by going from MP2 to CCSD(T) methods, as one might expect. The CCSD(T) predicted frequencies are nearly independent of basis set, which suggests that one may achieve satisfactory accuracy at a relatively low computational by implementing a small basis set (e.g., ccd) with the CCSD(T) approach.

The choice of basis set causes a 1-3 cm⁻¹ variation on the accuracy of the calculated frequency shifts for $Au_+(CO)^n$, n = 1-4, a negligible effect. Both MP2 and CCSD(T) correctly predict the trend in the magnitude of the frequencies shifts, but the MP2 calculations are only qualitatively correct. Hence, this suggests that CCSD(T) calculations are necessary to obtain frequencies that are within 10 cm⁻¹ of the experiment. Including anharmonicity in the frequency calculations should fur-

•	TABLE 3.2: Ex	sperimental and	Calculated Vibrat	ional Frequencies	for $\mathrm{Au}^{+}(\mathrm{CO})_{n}$ (n	= 1-6 in cm ⁻¹ ^a .	
			ţ	neory			
molecule	ccd/MP2	cct/MP2	ccq/MP2	ccd/CCSD(T)	cct/CCSD(T)	ccq/CCSD(T)	experiment
CO	2114	2122	2129	2144	2154	2164	2170^{b}
CO anharm	2088	2096	2102	2118	2128	2138	2143^{b}
$\mathrm{Au}^{+}(\mathrm{CO})$	2189	2194	2204	2247	2257		
Au ⁺ (CO) anharm	2157	2162		2216	2225		2195°
$\mathrm{Au}^+(\mathrm{CO})_2$	2207	2216	2226	2269	2280		2211 ^c
$\mathrm{Au}^{+}(\mathrm{CO})_{3}$	2163	2173		2229			2215
$\mathrm{Au}^{+}(\mathrm{CO})_{4}$	2149	2160		2218			2205
Au ⁺ (CO) ₅							2204
$\mathrm{Au}^{+}(\mathrm{CO})_{6}$							2203
^a Photodissociation 1	for n = 1, 2 cor	nplexes was not	observed. Calcı	ılations were done	at the MP2 or C	CSD(T) levels of 1	heory using ccd,
cct or ccq basis sets	on the C and O) atoms. Calcula	tions are harmon	uc unless otherwise	e noted with no v	ibrational scaling a	pplied. ^b Exper-
imental data for CO	are taken from	reference 103. $^{\circ}$	From reference	47, in condensed- ₁	ohase superacid n	nedia.	

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ther improve accuracy. But there are no available experimental data for the Au⁺(CO) complex' vibrational frequencies, and the high computational cost of VSCF calculations precludes the small corrections gained by including anharmonicity for the Au⁺(CO)_n, n = 3 and 4 computed frequencies. The frequency for Au⁺(CO) at the highest level here (2225 cm⁻¹) is slightly higher than that computed previously by Neumaier et al. (2211 cm⁻¹) at the DFT-BP86 level.⁶⁸ The value computed here is much greater than that reported by Lupinetti et al (2177 cm⁻¹) using a combination of CCSD(T) and MP2.¹⁰

Both the experimental and calculated data show that the C-O stretching frequency is higher in the bound complex that in the free CO molecule, with an interesting dependence of the magnitude of the frequency shift on the number of CO ligands bound to the gold cation. This trend in computed frequency shift can be summarized as $Au^+(CO)_2 > Au^+(CO) > Au^+(CO)_3 > Au^+(CO)_4$. The frequency of the C-O stretch increases upon CO binding to gold cation by about 100 cm⁻¹. There is an additional increase of ~25 cm⁻¹ upon binding of the second CO to the $Au^+(CO)$. Hence, there is an increase of ~125 cm⁻¹ in the C-O stretching frequency of $Au^+(CO)_2$ compared to that in the free CO molecule. Binding of the third CO significantly reduces the magnitude of the computed C-O stretching frequency shift to ~85 cm⁻¹. The fourth CO binding to the n = 3 complex leads to a small change of < 10 cm⁻¹. This suggests that there is a leveling off of the magnitude of the C-O stretch frequency shift in $Au^+(CO)_n$ complexes.

As noted above, we were unable to measure spectra for the n = 1 and 2 complexes, but these species have been studied in the condensed phase environment of a superacid matrix by Willner and Aubke.⁴⁷ In that study, the C-O stretching frequency for the n = 1 and n = 2 complex was reported to be 2195 and 2211 cm⁻¹, respectively, which are both considerably lower than the values computed here. But it is not clear what effect, if any, the superacid matrix has on these spectra. The computed vibrations can be compared directly to our gas-phase experiment in the case of the n = 3 and 4 complexes. At the highest level of theory (ccd/CCSD(T)), the harmonic frequency computed for the n = 3 complex is 2229 cm⁻¹, which is 14 cm⁻¹ higher than the experimentally observed value of 2215 cm⁻¹. For n = 4, the computed value is 2218 cm⁻¹, which is 13 cm⁻¹ higher than the observed value of 2205 cm⁻¹. These computed harmonic values are unscaled, and the approximate value and trends of the blue shifted vibrations match experiment well. We can use the Au⁺(CO) data, where both harmonic and anharmonic values were calculated, to derive a scaling factor to correct the larger species' spectra for the effects of anharmonicity. So doing results in a scaling factor of 0.986. Applying this factor to the ccd/CCSD(T) frequencies computed for the n = 3 and 4 complexes produces scaled frequencies of 2197 and 2186 cm⁻¹. These scales values are lower that the experimental values. Furthermore these scaled values are even further away from the observed vibrations than the unscaled values. Therefore we can conclude that there is no advantage in applying a scaling factor to the computed frequencies.

The blue-shifts in the vibrational frequencies occurring in these nonclassical carbonyl systems have been discussed extensively in the literature.⁶ The binding interaction is expected to involve σ -type donation from the 5 σ carbonyl HOMO and π -type back-donation in the 2π * LUMO. For other metal carbonyl complexes, the back-donation is expected to be a much more significant component in the binding, and subsequently the bond energies and frequency shifts.⁶ However, because the gold cation is a d¹⁰ configuration, back donation is inefficient. Early proposals for the origin of the shift to higher C-O stretching frequencies claimed that the 5 σ orbital of CO has partial antibonding character.⁶ If this is true, then OC \rightarrow Au⁺ σ donation would remove the electron density in this orbital, thus strengthening the bond, resulting in higher C-O stretching frequencies, as is observed experimentally. However, using a combination of CCSD(1) and MP2 methods, Lupinetti et al. investigated this proposed binding interaction carefully. In their study, they compared the effect of placing a charged atom at either end of the carbonyl.¹⁰ They report that attachment at the oxygen end of the carbonyl did not produce the same frequency shift as attachment at the carbon end. The suggested removal of 5σ antibonding character should have been possible in either binding configuration. Thus the explanation relying on a reduction of 5σ character is not the correct one. Instead, Lupinetti et al. suggested that an electrostatic orbital polarization effect is responsible for the C-O frequency blue shift. In the isolated CO, the bonding orbitals in the valence shell have more electron density on the oxygen. However, attachment of an ion on the carbon end of CO induces a polarization that effectively balances the orbital density on both atoms, thus enhancing the binding. This is the effect that is attributed to the blue-shift for nonclassical carbonyl systems.^{6,10} Consistent with this suggestion, the HCO⁺ ion, which also cannot have back donation, is calculated and observed to have a blue-shifted C-O stretch, but the HN₂⁺ complex, which has exactly balanced charge on its "ligand", does not (it is predicted and observed to be red-shifted).⁶

Finally, it is interesting to compare the vibrational shifts seen here for the atomic gold cation complexes to those reported previously for gold *cluster* ions. Fielicke et al. have previously investigated the gold cluster complexes containing 3-10 atoms⁴¹ and the corresponding gold cluster anion complexes containing 3-14 atoms.⁴² In these systems with differing numbers of CO ligands, the cations were found to have blue-shifted C-O stretching frequencies, relative to the free CO diatomic, while anions were found to have red-shifted vibrations, again relative to the free CO molecule. The anions have additional electron density, enabling efficient π back bonding. Thereby, electron density in the π^* LUMO of CO is increased, and the vibrational frequencies are driven to lower values. This is the so-called classical carbonyl behavior observed for the bulk of all other metals. In

the cationic gold clusters, the same kind of blue shift seen here is reported, but with less magnitude. As an example, the C-O stretch for $Au_3^+(CO)$ occurs at 2180 cm^{-1.41} Apparently, when the charge in a cluster cation is shared over more atoms, the polarization effect is diluted, and the blue shift in the C-O stretch frequency is less than that for the atomic ion complex. Consistent with this charge dilution effect, the blue shift becomes gradually less as larger gold cluster cation carbonyls are studied.⁴¹

3.5 Conclusions

Complexes of $Au^{+}(CO)_n$ have been generated with a laser vaporization source and investigated with infrared photodissociation spectroscopy and theoretical calculations at the MP2 and CCSD(T) levels of theory. Mass spectra and photodissociation patterns indicate that gas phase goldcarbonyl complexes have a preferred coordination number of two, which is consistent with the computed binding energies reported here. The gas-phase spectra of $Au^+(CO)_n$, n = 3-6, all exhibit significant blue-shifts from the free carbon monoxide stretch, as observed in both condensed phase measurement and matrix-isolation studies, indicating nonclassical carbonyl behavior. No gas phase experimental data is available for the n = 1 and 2 complexes. Single bands are observed for each of the complexes studied in the C-O stretching region, which is consistent with high symmetry structures. We can therefore conclude that $Au^+(CO)_3$ has a trigonal planar structure and $Au^+(CO)_4$ is tetrahedral. Calculations done at the CCSD(T) level of theory with cct basis sets for C and O atoms yield best agreement with experimental vibrational frequencies. More importantly, the theory and experiment show good agreement in the trends of the vibrational shifts.

The picture of the bonding in these complexes is one of a dative interaction in which the lone pair density from the carbonyl ligand is nominally donated into the empty s orbital of the gold cation. This ligand repulsion is minimized by s-d hybridization, which also enhances the binding strength. This interaction saturates at two ligands. The dominant effect of the electrostatic bonding polarizes the CO ligand, shifting its vibrational stretching frequency to higher values than those of the free CO diatomic. These effects have been discussed at length in previous theoretical work, and they have been reported experimentally for $Au^+(CO)_n$, n = 1 and 2, complexes in the condensed phase with counterions present. This combined experimental and computational study documents the expected trend in the bond energies and provides the first view of the frequency shifts for the larger n = 3-6 complexes. The blue shifts in these vibrations for atomic gold cation complexes are greater than those seen previously for carbonyl complexes of gold cluster cations.

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3.7 References

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CHAPTER 4:

GAS PHASE INFRARED PHOTODISSOCIATION STUDY OF $Pt^+(CO)_n$, n = 4-6COMPLEXES: CLASSICAL OR NONCLASSICAL METAL CARBONYL BEHAVIOR?¹

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4.1 Abstract

Complexes of $Pt^+(CO)_n$ are generated using a laser vaporization source coupled to a supersonic expansion. The complexes n = 4-6 are probed with infrared photodissociation spectroscopy in the vicinity of the free CO stretch (2143 cm⁻¹). No fragmentation was observed for the n = 1-3 complexes, indicative of their high binding energies, as seen in other work. The n = 4 complex produced a noisy spectrum and is expected to have a binding energy which would not result in fragmentation with a single ~2150 cm⁻¹ photon. Because of the high laser fluence conditions necessary to fragment the n = 4 complex, the suggestion here is that photodissociation occurs as a two photon process, which is corroborated by the binding energies computed and observed in the literature. The n = 5 and 6 complexes do efficiently fragment with a single photon absorption and their frequencies are slightly blue shifted (≤ 12 cm⁻¹) with respect to free CO. The single-peak spectra suggest high symmetry structures and the breakdown patterns of the ions gives evidence for a coordination number of four. The synergy in the metal-carbonyl bonding is discussed in light of the slightly-shifted vibrational frequencies.

4.2 Introduction

Transition metal(TM)-carbonyl systems have a rich chemical history that spans nearly 150 years.¹ There are numerous examples of TM-carbonyl complexes that have been synthesized and characterized throughout inorganic and organometallic chemistry.^{1,2} TM-carbonyl complexes are often used in synthesis and industrial catalysis.¹⁻³ Additionally, TM-carbonyls can serve as important fundamental models for complex systems such as chemisorption on metal surfaces.⁴ Infrared and Raman vibrational spectroscopy of metal carbonyls provides important information about their structures and bonding.⁵ Gas phase metal carbonyl ions have been studied extensively using mass spectrometry.⁶⁻⁸ Theory has probed the structures and bonding in these ions.^{7, 9-18} Bond energies have been determined, but there is much less data on their gas phase spectroscopy.¹⁹⁻²⁶ However, photoelectron spectroscopy has been employed to study a variety of metal carbonyl anions, providing vibrational information for the corresponding neutral ground states.²⁷⁻³⁰ Infrared spectroscopy of unsaturated neutral metal carbonyls isolated in rare gas matrices has been reported,^{8, 31-33} and infrared photodissociation measurements have been described for metal cluster carbonyl cations using free electron lasers.³⁴⁻³⁷ Our group recently reported an infrared photodissociation study of atomic gold-carbonyl cations in the gas phase using table-top infrared optical parametric oscillator laser systems.³⁸ In this study, we extend our investigations of TM-carbonyl species with such infrared lasers to investigate the carbonyl complexes of atomic platinum cations, $Pt^+(CO)_n$, n = 4-6.

The Dewar-Chatt-Duncanson model is typically used to describe the bonding in transition metal carbonyl compounds and complexes.^{1, 7, 8, 39, 40} In this paradigm, the metal-CO bond is understood as a synergistic relationship between two general types of interactions, σ -type donation and π -type back donation. The CO contributes electron density from its HOMO to the transition metal

on-axis, forming the dative σ bond, and removing electron density from the carbonyl. Donation of electron density from the d-shells of the metal into the LUMO of CO results in π back-bonding. In so-called "classical" metal carbonyls, the C-O stretching frequency is lowered, often significantly, relative to that in free CO (2143 cm⁻¹),⁴¹ and its bond lengthened due the gain of antibonding electron density in the LUMO on CO. The vast majority of transition metal carbonyl complexes demonstrate such classical behavior due to partially filled d orbitals that can contribute to significant π back bonding as evidenced by their red-shifts relative to free CO.^{18, 42-46}

Exceptions to a rule can often provide deeper insight into a bonding mechanism and examples are known of "nonclassical" carbonyl bonding.^{8, 35, 36, 38, 43-46} Nonclassical metal carbonyl systems usually include metals with filled d shells that are not able to donate or accept charge efficiently, such as noble metal atomic ions. Theoretical studies have discussed the origins of this vibrational blue shift, which appears to be found for only a few systems, including the Group 10 and 11 metal systems formed in condensed-phase superacid media.^{43,47} Indeed, the noble metal atomic ions are known to exhibit such nonclassical behavior in the condensed phase, and our work noted above reports the theory and blue-shifted spectra for gas-phase $Au^+(CO)_n$, n = 3-6, complexes.^{38, 45} Furthermore, noble metal cluster complexes with carbonyls have been studied in the gas phase using multiphoton infrared spectroscopy with a free electron laser.^{35, 36} For metal carbonyl systems with incompletely-filled d electronic shells, such as the atomic platinum cation, we might expect classical carbonyl behavior marked by a characteristic red-shift with respect to free CO. In fact, as discussed below, gas-phase platinum carbonyl cations demonstrate a small vibrational blue shift.

Platinum is an important metal forming a vital component of cancer-fighting drugs⁴⁸ and both industrial- and laboratory-scale catalysis.³ Platinum is well known as a particularly active cata-

lyst, and its activity is ubiquitous in helping to control emissions of automotive combustion gases.³ Indeed a platinum carbonyl salt was the first metal carbonyl isolated and studied in $1870.^{49.51}$ Furthermore, it has been shown that the platinum cation can activate methane for subsequent catalytic dehydrogenation in the gas phase.⁵² The intrinsic reactivity of a pure metal cluster or gas phase metal-ligand complex is difficult to measure. However, gas phase measurements of isolated metal systems using vibrational spectroscopy may be able to enhance our understanding of the structure and binding in these complexes. Microwave studies have examined low-frequency bending modes in neutral Pt(CO).⁵³ Condensed-phase vibrational spectra of dipositive platinum carbonyls display an increased stretching frequency at 2261 cm⁻¹ for metal-bound CO in highly acidic media.^{8, 32, 45, 54} Moreover, infrared studies exist of monocationic, neutral and anionic platinum-carbonyl complexes frozen in neon matrices. In one such study, Andrews and coworkers report observed vibrational frequencies of 2205, 2210 and 2208 cm⁻¹ for Pt⁺(CO)_a, n = 1-3, respectively.³²

Our research group has used resonance-enhanced infrared photodissociation spectroscopy to investigate a number of transition metal cation-ligand systems and to probe their gas-phase structures. We have reported infrared spectra for several different metal cations with multiple CO_2 ligands.^{55,57} We have studied acetylene bound to Ni⁺ to determine the coordination number as well as the structures of small complexes.⁵⁸ Numerous metal-water complexes have been investigate by our group.^{59, 60} We have measured infrared spectra for N₂ complexes, isoelectronic with CO, with V⁺ and Nb⁺.^{61, 62} Using the organic carbonyl acetone, we have measured the shifts associated with the carbonyl stretch upon binding to Mg⁺, Al⁺ and Ca⁺.⁶³ And as mentioned previously, we have reported significant blue-shifts for multiple CO ligands bound to atomic gold cation, labeling these complexes nonclassical carbonyls.³⁸ In the present study, we investigate the behavior of $Pt^+(CO)_n$, n = 4-6, complexes in the gas-phase using these same methods.

4.3 Experimental

Platinum-carbonyl cation complexes are produced by pulsed laser vaporization (355 nm; Spectra-Physics INDI 30-10) of a ¹/₈ inch platinum sample mounted in a rotating rod, pulsed nozzle source. The holder used in these experiments has the so-called cutaway configuration, and the entire apparatus has been previously described in detail.⁵⁷ The expansion gas is a mixture of 2-4 % CO in Ar, by partial pressure. A few drops of water are added to the gas lines to facilitate the growth of cationic metal-ligand complexes, as discussed elsewhere.⁵⁷ By changing the vaporization and/or pulsed nozzle parameters, various size distributions are produced. Figure 4.1 shows a typical mass spectrum obtained for complexes of the type $Pt^+(CO)_n$. These complexes are mass-selected and detected with a modified reflectron time-of-flight mass spectrometer. Mass spectra are recorded with a digital storage oscilloscope (LeCroy "WaveRunner" LT342) connected to a PC computer via a standard IEEE 488.2 interface. Tunable infrared radiation is produced with a specially designed infrared optical parametric oscillator/optical parametric amplifier (OPO/OPA) system (LaserVision) pumped with a high power Nd:YAG laser (Continuum 9010). The linewidth of the OPO is about 0.3 cm⁻¹ and the pulse energy is about 1 mJ in the region scanned for this experiment. Excitation of the mass-selected ions takes place in the turning region of the reflectron, and fragment mass analysis occurs in the flight tube section located after this. Monitoring the fragment ion yield as a function of the infrared frequency in the vicinity of the free C-O stretching vibration (2143 cm⁻¹) generates an infrared action spectrum.

Figure 4.1 Mass Spectrum of $Pt^+(CO)_n$. The smaller peaks are molecular clusters of $(CO)_n^+$ and $H_3O^+(CO)_n$. That platinum metal cation peak is off-scale.



4.4 Results and Discussion

The laser vaporization source efficiently generates different sizes of platinum-carbonyl cations as well as other species with much lower concentrations. Figure 4.1 shows the mass spectrum of $Pt^+(CO)_n$, for n up to about 24, where the platinum cation peak is off-scale. Depending on source conditions, complexes up to n = 30 can be grown, as discussed below; the focus of this study is for complexes with n = 4-6. The small mass progressions interspersed between the $Pt^+(CO)_n$ masses are the molecular complexes $(CO)_n^+$ (beginning with n = 4) and $H_3O^+(CO)_n$ (beginning with n = 4). The salient feature of the mass spectrum is the significantly enhanced intensity for the n = 4 mass channel, which occurs independent of the instrument's source or mass spectrometer focusing conditions. This observations suggests that the n = 4 complex is more stable than other complex sizes, which might indicate a preferred coordination number for gas phase platinum cations.

Traditional inorganic chemistry interprets the strongly bound, stable metal carbonyls in light of the 18-electron rule. In fact, nearly all transition metal carbonyl species strictly adhere to this rule. According to this rule, each CO molecule donates two electrons in a dative binding interaction. However, one well-known, notable exception to this rule is the neutral $V(CO)_6$ complex. This complex has 17 electrons, but its nearly-full d shell result in a chemically stable complex that is very close to the 18-electron count. While no stoichiometries of $Pt^+(CO)_n$ can yield exactly 18 valence electrons, the n = 4 complex has an electron count of 17, similar to that in the neutral vanadium carbonyl complex. The n = 5 complex has 19 electrons, which should result in a much less stable complex. Based on this rule, we can then suggest that the coordination number of the platinum cation with CO should be four. To investigate the cation coordination in more detail, we measured the fragmentation behavior of these complexes via photodissociation mass spectra, which is shown in Figure 4.2. For these measurements, a particular mass channel was selected and the infrared laser scanned in the region where the C-O stretching resonances are expected, until a photodissociation signal was found. Mass spectra were then recorded with the photodissociation laser "off" and subtracted from that recorded with the laser "on". The resulting difference spectrum shows the breakdown of a parent ion into fragment ions. In the case of the n = 1-3 complexes, no fragmentation signal could be found. We do expect that these metal complexes have infrared-active vibrations somewhere in this C-O stretching region. However, the lack of any observed photodissociation indicates that the platinum cationcarbonyl bonds for these smaller complexes are too strong to be broken by the energy of the infrared excitation. We then must conclude that the $Pt^+(CO)_n$, n = 1-3, bond energies exceed the infrared photon energy that would excite the C-O stretches in these complexes, i.e., they are greater than ~2150 cm⁻¹ (6.1 kcal/mol). Thus, we may surmise that those that do dissociate have CO binding energies that are less than the photon energy absorbed by each complex.

The larger complexes with n > 3 CO ligands do give a photodissociation signal. As indicated, there is only one fragment channel for each of these complexes. For the n = 4 complex, it was necessary that the photodissociation laser fluence be high to initiate the loss of CO, and as shown in the figure this complex has a poorer signal-to noise ratio than the larger complexes. For the n = 5 complex, the fragment channel is loss of a single CO. For the n = 6 complex, the sole fragment channel is loss of two CO ligands, with little or no single-CO loss channel present. Because the frequency shift in the C-O stretch for the n = 4-6 complexes is very nearly the same, we can suggest that the n = 5 and 6 have configurations in which the fifth and sixth CO do not bind directly to the metal ion, as discussed below. For the n = 5 and 6 complexes the infrared laser pulse energy em-

Figure 4.2 Difference mass spectra for the complexes $Pt^+(CO)_n$, n = 4-6. In all cases the mass depletion of the parent ion is off-scale. The fragmentation patterns of the larger complexes and the lower signal-to-noise for the n = 4 complex suggest a coordination number of four for platinum cation, as discussed in the text.



ployed here is approximately 1 mJ/pulse, with an unfocused \sim 4 mm diameter spot size, and these fragmentation channels vary with the laser pulse energy consistent with a single photon process. Fragmentation for the n = 4 complex could only be detected with a poor signal-to-noise ratio with a focused, high fluence IR laser beam.

To measure vibrational spectra for these complexes, we record the wavelength dependence of their fragmentation yields. As mentioned, for the n = 1-3 complexes, no photodissociation was observed, and so we could not study these systems in this way. This is not surprising, as Armentrout and coworkers have measured binding energies using collision induced dissociation (CID) for Pt⁺(CO)_n, and they report energies of 50.6 (17 700 cm⁻¹), 46.0 (16 100 cm⁻¹), 23.5 (8240 cm⁻¹) and 12.7 (4450 cm⁻¹) kcal/mol for the n = 1, 2, 3 and 4 complexes, respectively.²³ Clearly with these high binding energies, single photon photodissociation in the C-O stretching region is impossible. Multiphoton absorption is not a tenable route to photodissociation here as more than 15 photons would be required for the n = 3 complex, and this process is inefficient due to the low laser power available. The usual method for investigating strongly-bound systems like these is rare-gas "tagging", in which a more weakly bound rare gas atom is added to the complex to enhance its photodissociation yield.^{57, 59, 63-66} We were able to tag a small amount of the n = 1-3 complexes with argon atoms but saw no fragmentation, so were to study these complexes in this way. While we were unable to obtain a computed or measured value for the binding energy of platinum cation to Ar, the neutral PtAr dimer is calculated to have $D_{e} = 6.99 \text{ kcal/mol} (\sim 2447 \text{ cm}^{-1}).^{67}$ This binding exceeds the energy of a single 2150 cm⁻¹ (6.1 kcal/mol) photon. Moreover, it is reasonable to expect that the binding energy of the cationic Pt⁺Ar dimer should be appreciably higher than that for the neutral dimer. So, it is not surprising that we were unable to observe fragmentation for the Ar-tagged small complexes.

Figure 4.3 Infrared resonance enhanced photodissociation spectra for $Pt^+(CO)_n$, n = 5 and 6. No photodissociation was observed for the n = 1-3 complexes, and the spectrum of the n = 4 complex was noisy with apparent multiphoton absorption (discussed in the text). The free CO stretch (2143 cm⁻¹) is indicated with a dashed vertical red line.



Tagging with the rare gas neon would probably improve the photodissociation yield, as it is less polarizable than Ar and thus generally has a weaker binding to cations. But we were not able to successfully tag any complex with Ne. Therefore, we were unable to obtain any spectra for the n = 1-3complexes.

The n = 4-6 complexes do fragment in the 2150 cm⁻¹ region. The resonance-enhanced photo dissociation spectra for these complexes are presented in Figure 4.3. The n = 4 complex did fragment, but it spectra was very noisy and is discussed in more detail below. In the figure, the fundamental frequency for the C-O stretch in the isolated CO diatomic molecule (2143 cm⁻¹) is indicated with a vertical dashed red line. All of these complexes have spectra with single peaks that are slightly shifted to higher frequency than this value. The single peak in the C-O stretching region suggests that these complexes have high symmetry, with equivalent CO ligands, as more than one infrared band would otherwise be expected here. Table 4.1 presents the observed vibrational frequencies and their shifts relative to the free CO stretch. The n = 4 complex has a poor signal-to-noise ratio with a broad single band at 2155 cm⁻¹, which is shifted 12 cm⁻¹ to the blue from the free CO band. This is the largest blue shift seen in this study. The n = 5 and 6 complexes each have single bands each at nearly the same positions as the n = 4 complex. Most likely, the spectra recorded for these complexes is actually that of Pt⁺(CO)₄ with the fifth and sixth CO ligands binding in a CO-CO interaction rather than directly to the metal. Therefore, we can suggest that the bonding motif for the n = 5 and 6 complexes is actually that of 4+1 and 4+2 CO ligands, respectively. For the n = 5 complex the resonance lies at 2155 cm⁻¹, corresponding to a vibrational shift of 12 cm⁻¹ to the blue of free CO. The n = 6 complex displays a resonance at 2153 cm⁻¹, which is blue-shifted 10 cm⁻¹.

	binding energy,	vibrational frequency (cm ⁻¹)		
complex	(kcal/mol)	calculated	observed	shift , Δν
Pt ⁺ (CO)	50.6ª	2262ª	2205 ^b	62
$Pt^{+}(CO)_{2}$	46.0ª	2262ª	221 0 ^b	67
$Pt^{+}(CO)_{3}$	23.5 ^ª	2243 ^a	2208 ^b	65
$Pt^{+}(CO)_{4}$	12.7 ^a	2212 ^ª	2155, 2155, 2153°	12, 12, 10

TABLE 4.1 Observed vibrational frequencies and their shifts relative to free CO (2143 cm⁻¹).

^a taken from Reference 23

^b in a frozen Ne matrix, Reference 32

^c Frequencies for the n = 4, 5 and 6, respectively from this work. The n = 5 and 6 complexes exhibit spectra are that of the n = 4 complex with second-sphere CO ligands. As noted above, blue-shifted CO vibrations have also been documented previously for the condensed phase $Pt^{2+}(CO)_4$ complex in acidic environments.⁴⁶ While a direct comparison is not possible due to the difference in charge state, it is reasonable to expect larger blue-shifts for the dicationic platinum species than the monocations in this study. Also, findings have been reported on cationic platinum carbonyl complexes isolated in rare gas matrices. In the condensed phase, the measured blue-shift is 118 cm⁻¹ for the n = 4 dicationic complex. Our monocation gas-phase spectra begin with the n = 4 complex, and the qualitative trend of blue-shifted CO stretches is evident, but due to differing charge states, no further conclusions may be drawn. In matrix-isolation studies, shifts of 62, 67 and 65 cm⁻¹ were observed for the n = 1, 2, and 3 complexes, respectively. Again, we do not have a direct comparison to our values for the n = 4-6 complexes. However, the qualitative agreement in blue shift upon binding to cationic platinum is present.

Armentrout et al. used CID to determine the binding energy of the last CO for the n = 4 complex to be 12.7 ± 1 kcal/mol (4436 ± 400 cm⁻¹), as mentioned above.²³ Likewise, using density functional theory, they calculated a binding energy for the last CO to be 9.7 kcal/mol (3402 cm⁻¹), which is in reasonable agreement with their experimentally-determined value. But in a poor signal-to noise spectrum for the n = 4 complex, we see fragmentation near 2150 cm⁻¹ (6.1 kcal/mol). Unlike the n = 5 and 6 complexes, this photodissociation yield could only be obtained at very high laser fluence. The IR laser was double-passed through the reflectron with a concave focusing mirror to increase the radiation density in the turning region. Hence we may have been observing fragmentation consistent with a two photon absorption. This seems likely as two resonant IR photons would have energies comparable to the computed and measured values in the CID study. Because multiphoton absorption efficiency is poor, a low photodissociation yield and noisy spectrum for the n = 4 complex result. No binding energies are available for the n = 5 and 6 complexes, but the low IR

laser fluence photodissociation breakdown patterns shown in Figure 4.2 indicate that they both fragment to the n = 4 terminal ion. We can then say that the binding energy of these fourth and fifth ligands has an upper limit of 2150 cm⁻¹ (6.1 kcal/mol).

If the coordination number of the gas-phase Pt cation is four, as suggested by Armentrout and coworkers and our photodissociation breakdown patterns, then the fifth and sixth ligands can be thought of as binding in the second coordination sphere with a purely ligand-ligand interaction. Therefore the spectra recorded for the n = 5 and 6 complexes is actually that of $Pt^+(CO)_4$ with additional "tagging" CO molecules, as mentioned above. The binding energy of the CO dimer is reported to be 155 cm⁻¹,⁶⁸ and these weak interactions lead to efficient fragmentation with a single \sim 2150 cm⁻¹ photon, as observed. In our previous work we have seen that when a ligand begins binding in the second sphere, an additional band grows in that is very near the free molecule's vibrational frequency. However, no additional bands are observed here. We saw this same behavior in our $Au^+(CO)_n$ IR study as well as our studies of transition metal cations with N_2 .^{38, 61, 62} As discussed in those papers, this phenomenon is not surprising. In the case of CO, the dipole moment is small (0.11 D) and its infrared intensity may be negligible compared to the metal-bound carbonyl stretches. In the case of the metal- N_2 complexes, the N_2 is only IR active upon binding to the metal ion. Since the unbound molecule has no dipole moment and is not IR active except when bound to the metal, its IR intensity would limit detection. Based on the enhanced ion intensity for the n = 4 complex in the mass spectrum and the photodissociation breakdown patterns, we concur with the above-mentioned Armentrout et al. paper that the coordination number is four for gas phase platinum cation and that it possesses a highly symmetric geometry.

Each of the spectra recorded for the n = 4-6 complexes exhibit only one band, indicative of a highly symmetric structure for the direct ligand-to-metal $Pt^+(CO)_4$ complex. The most likely structure for this complex is then either tetrahedral or square-planar. In fact, Armentrout et al. have determined that the n = 4 complex is square planar with a slight distortion towards tetrahedral.²³ They argue that the slight distortion is the result of four CO ligands avoiding direct interaction with the d_{x2-y2} orbital, which contains the unpaired electron in the d⁹ ion. Based on our spectra, we can only conclude that the n = 4 complex has a highly symmetric structure.

The shifts to higher vibrational frequencies occurring in nonclassical systems have been discussed extensively in the literature. The binding interaction in normal metal carbonyl systems is expected to involve σ -donation from the 5 σ HOMO and metallic π back-donation into the $2\pi^*$ LUMO on CO. As noted for most other metal carbonyl complexes, the back-donation is a much more significant factor in the bond energies and frequency shifts. However, because of platinum cation's incompletely filled d⁹ configuration, back-donation, while clearly present, is sufficient only to mostly offset the electrostatic σ -type interaction. As discussed in our work with gold carbonyl, early suggestions for the origin of the shift to higher C-O stretching frequencies claimed that the 5σ orbital of CO has partial anti-bonding character.⁷ However, Lupinetti et al. investigated this proposal with studies that compared the effect of placing a charged atom at either of the two ends of the carbonyl and found that attachment at the oxygen end did not produce the same frequency shift as attachment at the carbon end.¹² Upon binding of a CO to a cation, the removal of 5σ anti-bonding character in the HOMO of CO should have been possible in either configuration, which does not agree with the Lupinetti et al. findings. Instead, they were able to show that an electrostatic orbital polarization effect is responsible for the C-O blue shift. In the isolated CO molecule, the bonding orbitals in the valence shell have more electron density on the oxygen, and are thus unbalanced,

which limits the effectiveness of the binding. However, attachment of an ion on the carbon end of CO induces a polarization that effectively balances the orbital density on both atoms, thus enhancing the binding. This is the effect that is now generally attributed to cause the C-O stretch to shift to higher frequencies in these non-classical systems.

However, unlike our findings on gold carbonyl complexes, the shifts observed here are only slight ($\leq 12 \text{ cm}^{-1}$). This points to a bonding interaction that includes more than a simple electrostatic σ -type interaction. Back donation by the platinum cation's incompletely filled d orbitals apparently causes a near-canceling effect of the blue shift on the C-O stretching frequency. As Strauss and coworkers suggest, simple labeling of classical or nonclassical based on vibrational shifts alone is not sufficient to understand the real interplay in the two bonding motifs.¹³ *All* metal carbonyl systems have σ -type interactions which are nonclassical in nature. However, *most* metal carbonyl systems also have dominant off-axis back bonding effects that usually result in red-shifted vibrational spectra. In the case of these larger gas phase platinum carbonyls, these effects almost cancel and it is not adequate to simply label these systems nonclassical based on their ~10 cm⁻¹ blue shift alone. To further understand gas phase Pt⁺(CO)_n complexes, a higher-level theoretical treatment of these two primary interactions could better quantify their relative contributions, although the platinum ion does present significant challenges to theory because it is open-shell and requires a relativistic treatment.

4.5 Conclusions

Complexes of the form $Pt^+(CO)_n$ have been generated with a laser vaporization source and investigated with infrared photodissociation spectroscopy. Mass spectra and photodissociation patterns indicate that gas-phase platinum-carbonyl complexes may have a preferred coordination number of four, which is supported by an electron count of 17, close to the 18-electron rule requirement. No fragmentation was observed for the $Pt^{+}(CO)_n$, n = 1-3 complexes due to high binding energies for the complex and their Ar tagged counterparts. The vibrational spectra of the n = 4-6 complexes all exhibit slight blue-shifts from the free carbon monoxide stretch, qualitatively consistent with previous condensed-phase measurements and matrix-isolation studies. Single bands are observed for each of the complexes studied in the C-O stretching region, consistent with high symmetry structures. In support of Armentrout and co-workers' CID and DFT studies, we can therefore conclude that $Pt^+(CO)_4$ has a near square-planar structure. The n = 4 complex yielded a noisy photodissociation spectrum with most likely a two-photon absorption. Such a multiphoton process in this complex is in excellent agreement with the binding energy determined by Armentrout and coworkers in CID measurements. The n = 4 and 5 complexes fragment with efficiency in a single photon process. The improved signals for these complexes, as well as the enhanced intensity for the n = 4complex in the mass spectrum and the breakdown patterns for these larger complexes suggest that the coordination number for gas phase Pt^* is indeed four, in agreement with the work of Armentrout's group.

The magnitude and direction of a complex's vibrational shift relative to the free CO molecule is a result of a synergistic effect of electrostatic σ -type bonding and π back bonding from the metal d-orbital electrons to the antibonding orbitals on CO. The bonding in these complexes is one of a dative interaction in which the lone pair density from the carbonyl ligand is nominally donated into the empty s orbital of the Pt⁺ ion. The electrostatic bonding polarizes the CO ligand, shifting its vibrational frequency to values higher than those in the free CO molecule. However, this effect is largely offset by back donation of partially filled d orbital of Pt⁺ to the π^* orbital of CO. Thus the small magnitude of the observed blue-shift in these complexes suggests a system in which the effects attributed to the Dewar-Chatt-Duncanson bonding model are largely canceling. The interplay of these bonding motifs has been discussed at length in previous theoretical work. This experimental study provides the first look at the frequency shifts for the n=4 complex.

4.6 Acknowledgements

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CHAPTER 5

IR SPECTROSCOPY OF M⁺(acetone) COMPLEXES (M = Mg, Al, Ca): CATION-CARBONYL BINDING INTERACTION¹

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5.1 Abstract

 M^+ (acetone) ion-molecule complexes (M = Mg, Al, Ca) are produced in a pulsed molecular beam by laser vaporization and studied with infrared photodissociation spectroscopy in the carbonyl stretch region. All of the spectra exhibit carbonyl stretches that are shifted significantly to lower frequencies than the free-molecule value, consistent with metal cation binding on the oxygen of the carbonyl. Density functional theory is employed to elucidate the shifts and patterns in these spectra. Doublet features are measured for the carbonyl region of Mg⁺ and Ca⁺ complexes, and these are assigned to Fermi resonances between the symmetric carbonyl stretch and the overtone of the symmetric carbon stretch. The carbonyl stretch red shift is greater for Al⁺ than it is for the Mg⁺ and Ca⁺ complexes. This is attributed to the smaller size of the closed-shell Al⁺, which enhances its ability to polarize the carbonyl electrons. Density functional theory correctly predicts the direction of the carbonyl stretch shift and the relative trend for the three metals

5.2 Introduction

Metal ion complexes in the gas phase may serve as model systems for metal ion solvation,¹⁻³ metal-ligand interactions,²⁻⁶ and the binding of metal cations in biological systems.⁷⁻⁹ Many bio-molecules and proteins possess sites for metallic binding facilitating enzymatic activity and enhancing metabolic function. In such biological systems, the cation often binds to the carbonyl of the amino acid.⁷⁻¹⁸ Vibrational spectroscopy is often used to investigate structure and bonding, but in biological systems, the carbonyl region of the infrared spectra (known as the "amide I") is often cluttered by absorptions from other functional groups on the protein.^{17, 18} In the infrared study presented here, we pinpoint the carbonyl-cation interaction with cation-acetone complexes of magnesium, aluminum and calcium in the gas phase. By probing the spectroscopy in the stretch region of the carbonyl, we investigate the effects of cation binding for different metals and compare with theory to elucidate the structures of these complexes.

There has been much previous work with metal ion complexes of magnesium, aluminum and calcium using mass spectrometry.¹⁹⁻²⁸ To obtain dissociation energies for these metallic complexes, collision-induced dissociation has been used.²¹⁻²⁸ Complexes of Mg⁺ and Ca⁺ have served as ideal systems to probe with electronic spectroscopy because of their convenient, low-energy p←s transition.^{2, 29-60} Mg⁺(acetone) has been studied with fixed frequency photodissociation at 355 nm.³² In contrast, complexes of aluminum have less accessible electronic spectra,⁶¹ but tend to have low ionization potentials,⁶²⁻⁶⁵ which are conducive for ZEKE or MATI photoelectron spectroscopy studies.⁶³⁻⁶⁹ More recently, complexes of Mg⁺, Al⁺ and Ca⁺ with various ligands such as CO₂, H₂O, CH₃OH and NH₃ have been probed with infrared photodissociation spectroscopy.⁷⁰⁻⁷⁸ Lisy and coworkers have studied the infrared spectroscopy of alkali cation-acetone complexes in the C-H stretch region.⁷⁹ Furthermore, ab initio calculations have investigated the energetics of bonding and the structures of these metal ion-molecule complexes.^{45-50, 70, 73-78, 80-85, 86-98}

Until recently, applications of infrared spectroscopy for the structure determination of cation-molecule species have been rather limited because tunable infrared light sources were not generally available. Previous studies have employed bench-top optical parametric oscillator/optical parametric amplifier (OPO/OPA) systems producing tunable light in the near-infrared regions of the spectrum, from 4500 to about 2000 cm⁻¹,⁷⁰⁻⁷⁹ but the lower frequency region (< 2000 cm⁻¹), the so-called fingerprint region, was limited to large and expensive free-electron lasers (FELs). FELs have been used recently to study amino acids or peptides bound to metal cations.⁹⁹⁻¹⁰⁵ But relatively recent developments have extended the infrared range of bench-top OPO/OPA systems to ~700 cm⁻¹ using difference-frequency mixing in AgGaSe₂ crystals.^{106,107} Johnson and co-workers have employed this technology recently to study hydroxide-water anions and protonated water clusters.¹⁰⁸⁻¹¹⁰ In the work presented in this chapter, we use the extended IR tuning range afforded by the AgGaSe₂ crystal to probe metal cation-molecular complexes for the first time. We provide here a study of cation-acetone complexes probing the carbonyl stretch regions near 1700 cm⁻¹. In conjunction with theoretical calculations, we investigate the structures and bonding interactions of magnesium, aluminum and calcium cation-acetone complexes.

5.3 Experimental

Metal ion complexes with acetone are produced by pulsed laser vaporization (355 nm; Spectra-Physics Indi 30-10) of the respective metal rod samples in a rotating rod, pulsed nozzle source.², ⁷² Acetone is added to the argon expansion gas at ambient pressure and temperature. In the source, many species form and are jet-cooled, including complexes of the form $M^+(acetone)_n$ for n = 1-25 and $M^+(acetone)_nAr_m$ for n = 1-10 and m = 1, 2. These complexes are analyzed with a reflectron time-of-flight mass spectrometer, as described previously.^{2,72} Individual species can be mass selected for isolation and study. Figure 5.1 shows a typical mass spectrum for $M^+(acetone)_n$ where in this case M = Al. In Figure 5.1, source conditions are chosen such that no aluminum cation is produced, as shown. The mass peaks interspersed throughout the lower mass region include various complexes of $Al^+(acetone)_n$ with water and/or argon.

Tunable infrared radiation is produced with a specially designed infrared OPO/OPA system (LaserVision) pumped by a high-power, injection-seeded Nd:YAG (Continuum 9010) laser at 10 Hz repetition rate. Approximately one-third of the total pump energy (~600 mJ/pulse) is converted to the first harmonic of the Nd:YAG (532 nm) to pump the oscillator section of this system, which employs two KTP crystals. The remaining pump energy is mixed with the idler from the oscillator stage in two pairs of KTA crystals generating a signal (2000-4500 cm⁻¹) beam and an idler (5000-7500 cm⁻¹) beam. These beams are subsequently difference frequency mixed in an AgGaSe₂ crystal (LaserVision, 7 x 7 x 25 mm; 54° cut) producing the desired output near 1700 cm⁻¹ with an energy of about 250 μ J/pulse. The crystal of this particular cut provides useful IR over the range of about 700 to 1850 cm⁻¹. We performed scans here for all three complexes in the region 1550 to 1850 cm⁻¹, where the carbonyl stretch resonances are expected.

Density functional theory (DFT) calculations (Gaussian 03W)¹¹¹ were carried out at the B3LYP level using the 6-11+G** basis set on the M⁺(acetone) and M⁺(acetone)Ar complexes.^{112, 113} Vibrational scaling factors in the range of 0.96-1.00 were investigated to determine the best value appropriate for these metal cation-carbonyl complexes.

Figure 5.1 Typical mass spectrum for $M^+(acetone)_n$ complexes showing additional clustering with argon and water in the low masses for M = Al. Source conditions were chosen such that no aluminum cation was produced.



5.4 Results and Discussion

The laser vaporization source efficiently produces ample amounts of the M⁺(acetone)_n complexes for study here as well as tagged species with one or more argon atoms. The metal cation-acetone binding energy has been determined previously by both experiment and theory for these three metals.^{28, 81, 98} As shown in Table 5.1, these energies are more than 40 kcal/mol (14 000 cm⁻¹). Hence infrared excitations near 1700 cm⁻¹, the fundamental frequency of the carbonyl stretch, do not have enough energy to break these bonds. Thus we must use the technique of rare gas atom tagging with argon to achieve detectable photodissociation with our instrument.^{70-74, 76-78, 108-110, 114-118} Table 5.1 also presents the binding energy of argon to the metal cations, and in every case the known binding energy in the M⁺-Ar diatomic molecules is much less than 1700 cm⁻¹. Hence we expect that the argon binding energy in the M⁺(acetone)Ar complexes will also be less than carbonyl stretch frequency. And we do observe that all three M⁺(acetone)Ar complexes dissociate efficiently with infrared excitation in this region by losing the argon atom.

Figure 5.2 shows the infrared photodissociation action spectra of the three M^+ (acetone)Ar complexes, as measured in the argon-loss mass channel. As shown, all three systems exhibit resonances near 1700 cm⁻¹. No other resonances were observed in the region scanned, 1550 to 1850 cm⁻¹. The carbonyl stretch in the free acetone molecule occurs at 1731 cm⁻¹,¹¹⁹ which is indicated in the figure with a vertical blue dashed line. As shown, the resonances in the metal cation-acetone complex all occur at lower frequencies than the value for the free molecule. The dissociation yield is greater for the Mg⁺ and Al⁺ complexes than for the Ca⁺ complex. This accounts for the different relative signal/noise levels in these three spectra. Two bands are found in this region for the Mg⁺ and Ca⁺ complexes, whereas the Al⁺ complex has only one. However, the Al⁺ complex shows a
	energy (kcal/mol)	
complex	theory	experiment
Mg ⁺ (acetone)	41.3ª	41.4 ^b
	45.6°	
Al ⁺ (acetone)	41.5 ^d	
	42.7°	
Ca ⁺ (acetone)	41.0 ^c	
$\mathrm{Mg}^{+}\mathrm{Ar}$		3.70 (1295 cm ⁻¹) ^e
Al ⁺ Ar		2.81 (982 cm ⁻¹) ^f
Ca ⁺ Ar		2.00 (700 cm ⁻¹) ^g

TABLE 5.1Binding Energies of Complexes Relevant to the M⁺(acetone) Study.

^a Reference 99.

^b Reference 27.

^c This work.

^d Reference 81.

^e References 34, 35.

^f Reference 62.

^gReference 39.

Figure 5.2 Infrared photodissociation spectra of Mg^+ , Al^+ and Ca^+ complexes with acetone in the carbonyl stretching region. The argon-tagged complex was mass-selected, and the channel corresponding to loss of argon was recorded. The blue dashed line indicated the free-acetone stretch. The red lines indicate the predicted C=O stretch frequency from density functional theory calculations using a scaling factor of 0.990.



greater shift with respect to free acetone than the bands in the Mg^+ and Ca^+ spectra. To understand these spectra more fully, we consider the origin of the red-shifted bands and the doublet structure present for the Mg^+ and Ca^+ complexes, but absent from the Al^+ complex.

Upon binding to a metal, it is often seen that the vibrational frequencies of molecular ligands are red-shifted in frequency compared to those same vibrations in the corresponding free molecule. In conventional inorganic and organometallic chemistry, this phenomenon is observed for the bulk of all metal-carbonyl complexes in the condensed phase (so-called classical metal carbonyls).^{120, 121} Our group has observed similar trends for isolated gas-phase species, where the ligand was acetylene,^{122, 123} benzene,¹²⁴ water,¹²⁵⁻¹²⁷ or nitrogen.^{128, 129} Hence the strong shift of the carbonyl stretch observed here is consistent with a metal ion binding to the carbonyl of acetone, as one would anticipate from electrostatic considerations. In all of these systems, the cation withdraws bonding electron density from the on-axis highest occupied molecular orbitals of the ligand in the region of the cation attachment via σ donation. In transition metals, π back bonding may also be present, which offers d-electron density to low-lying off-axis antibonding orbitals on the ligand, thereby weakening the ligand's bond and subsequently its stretching frequency. However, these three metals studied have no partially filled d orbitals, and σ -type donation is the sole component for interaction with the acetone molecule. If these metal ions bind to the carbonyl of acetone, then the orientation is different from conventional metal-carbonyl complexes but the mechanism of charge transfer should be similar. The highest occupied molecular orbital of acetone is the nominally non-bonding b₂ orbital containing the oxygen lone-pair electrons, but this orbital also has partial binding character. The next lowest π -bonding b₁ orbital has density in the same spatial region. Binding on the oxygen end of the acetone carbonyl can polarize both of these orbitals. Therefore, we suggest that the met-

complex	M ⁺ -L Binding Energy, D _e (kcal/mol)	vibrational	frequency (cm ⁻¹)
Mg ⁺ (acetone)	45.6	M ⁺ -L stretch	309
		sym. C-C-C- str.	839
		C=O stretch	1680 (1663)
$\mathrm{Al}^{+}(\mathrm{acetone})$	42.7	M ⁺ -L stretch	283
		sym. C-C-C- str.	842
		C=O stretch	1630 (1614)
Ca ⁺ (acetone)	41.0	M ⁺ -L stretch	255
		sym. C-C-C- str.	831
		C=O stretch	1686 (1669)

TABLE 5.2 Energetics and Selected Vibrational Frequencies Calculated with Density Functional Theory for These Metal Cation-Acetone Complexes^a

^a The C=O frequencies in parentheses are those resulting from using a scaling factor of 0.990.

al ion binding to the carbonyl of the acetone molecule withdraws bonding electron density from the carbonyl moiety, and this action is observed as a lower frequency of acetone's carbonyl stretching vibration relative to the free molecule.

To be more quantitative about these vibrational shifts, we have investigated each of these complexes with density functional theory (DFT) calculations. We have studied both the neat $M^+(acetone)$ complexes as well as those tagged with argon. These data are summarized in Table 5.2. We find lowest energy structures for all complexes that have the metal cation binding on the oxygen cation, maintaining the overall C_{2v} symmetry of the complex, as shown in Figure 5.3. Although dissociation energies with DFT are not expected to be quantitative, the complex binding energies follow the trend $Mg^+ > Al^+ > Ca^+$. In the case of the Mg^+ complex, our binding energy is comparable to, but slightly higher than, the value calculated previously,⁹⁸ and it is in reasonable agreement with available experiments.²¹ The argon complexes each bind the rare gas on the metal ion. There are only slight energy differences between configurations with the rare gas on the C₂ axis in a linear O– M^+ -Ar configurations, as opposed to a bridging structure with it interacting with both the metal ion and a C-H hydrogen. For Mg⁺ and Al⁺, the argon bridging configurations are preferred, whereas Ca⁺ prefers the linear O- M^+ -Ar configurations in our previous work.⁶⁶⁻⁷⁴

The DFT frequencies of the acetone-based vibrations in all three complexes are virtually unchanged (shifts of 1-2 cm⁻¹) by the addition of the argon, regardless of its position. The carbonyl stretch frequency calculated for each complex is shown in Figure 5.2 as a vertical red bar. As indicated, DFT predicts that the carbonyl stretch undergoes a red shift upon binding to each of these metal cations. The relative amount of the red shift calculated (greater for the aluminum complex Figure 5.3 Structures calculated with DFT for the three metal cation-acetone complexes (metals are indicated by green) and their argon (blue) tagged complements. The structural parameters are given in the accompanying tables.

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9	
<u>e</u>	2

M^+	M ⁺ -O (Å)	C=O (Å)	C-C-C Angle
Mg	1.975	1.245	119.3°
AĪ	1.943	1.253	120.0°
Ca	2.217	1.241	118.9°



M^+	M ⁺ -Ar (Å)	M ⁺ -O (Å)	C=O (Å)	C-C-C Angle
Mg	4.314	1.977	1.244	119.3°
Al	4.579	1.943	1.253	120.0°
Ca	3.958	2.217	1.241	118.9°

than for the other two complexes) is also consistent with the experiment. However, the quantitative positions of the vibrational bands calculated depend on the vibrational scaling factor applied, as discussed below.

DFT theory computes harmonic vibrational frequencies that are expected to be higher than the actual anharmonic vibrations in these molecules. To compensate for this discrepancy, a scaling factor is usually applied. Comparing our DFT calculation for the free-acetone carbonyl stretch to the experimentally observed value for this vibration, we derive a scaling factor of 0.969. However, application of this multiplier to the metal ion complexes' DFT-calculated vibrations leads to an exaggerated prediction for the red shift of the carbonyl vibration in all three systems. Such application yields theoretical frequencies that fall 20-45 cm⁻¹ lower than the experimentally observed values. This overcorrection to the predicted frequencies is surprising, as DFT frequencies scaled similarly have led to near-perfect agreement with the our previously measured vibrational spectra for other ligands in higher frequency regions of the spectrum (> 2000 cm^{-1}).^{70-74, 122-124, 127, 128} It is well known that scaling factors become closer to unity as the frequencies of the vibrations become lower.¹³⁰ It is not obvious what scaling factor is appropriate here because there have been few previous studies to similar systems. Furthermore, scaling factors derived from organic ligands may pose problems when applied to inorganic complexes. The unscaled values for the carbonyl stretch frequencies we calculated are presented in Table 5.2. We experimented with different trial values for the scaling factor to investigate the appropriate value to use for these systems. We find that a value of 0.990 leads to good agreement between experiment and theory for all three complexes. This value is shown with the red bars in Figure 5.2. This same problem of carbonyl scaling factors has been recognized already in one previous infrared study of cationic amino acid and peptide ions.¹⁰¹

The doublet features observed here for the magnesium and calcium complexes can be interpreted with the aid of theory. As shown in Figure 5.2, only one infrared band is expected for each carbonyl resonance. We explored different binding configurations for the metal ion interactions with acetone and with argon, but in each case only one structure is found to lie at low energy. Hence, this effectively rules out different isomeric structures as the source of the multiplet bands. We also considered the possibility of the presence of both enol- and keto-tautomers as a source of two isomeric structures giving rise to the doublets. But for all of these complexes, our DFT calculations show that the enol species lies at significantly higher energies (~ 10 kcal/mol) than the keto form and is therefore not likely to be present. A final possibility for the multiplet structure near the carbonyl stretch is a Fermi Resonance. Table 5.2 shows the frequencies calculated for other relevant vibrations of these complexes. Fermi resonances may occur whenever there is an accidental neardegeneracy of any two (or more) vibrational states having the same symmetry and frequency. In this particular system, a₁ vibrational states that can couple with the carbonyl stretch may result from fundamentals or combinations of a_1 modes or overtones of any modes regardless of their symmetry. Of particular interest here, the symmetric C-C-C carbon stretch has the same a1 symmetry as the carbonyl stretch, and the overtone of this mode is almost exactly degenerate (within about 20 cm⁻¹) of the carbonyl stretch for the Mg⁺ and Ca⁺ complexes. In the case of the aluminum complex (where the carbonyl is much more red shifted) this combination is not nearly as close (the C=O stretch vibrations is more than 50 cm⁻¹ lower than the carbon stretch overtone). We therefore assign the multiplet structure seen for the Mg⁺ and Ca⁺ complexes but not for Al⁺ complex to a Fermi resonance between the carbonyl stretch and the symmetric carbon stretch overtone. To confirm this possibility, we measured the spectrum for the Mg⁺ complex with the ¹³C isotopically substituted at

the carbonyl carbon. The ¹³C isotope substituted-acetone is shown above the ¹²C species in Figure 5.4 below. In the ¹³C-substituted complex, a doublet is seen again, but both members are shifted to the red compared to their positions in the unsubstituted species, and their relative intensities are changed. This behavior is consistent with a Fermi resonance, confirming this as the most likely assignment for the doublets. We therefore take the average values of the doublets seen for the Mg⁺ and Ca⁺ complexes as approximate measures of the actual carbonyl stretch frequencies.

Both the experiment and theory show a much greater shift of the carbonyl stretch of acetone in the Al⁺ ion complex compared to that of either Mg⁺ or Ca⁺. As noted above, the red shift of this vibration is associated with a charge-transfer effect caused by the cation polarizing the slightly bonding lone pair electrons on the carbonyl. The electrostatics of such a charge induction are favored when the charge is "focused" into a small volume so that it more closely resembles a point charge. With its closed-shell configuration, Al^+ (3s²) has a smaller ionic radius (72 pm) than either Mg⁺ (82 pm) or Ca⁺ (118 pm),¹³¹ both of which have the ns¹ open-shell configurations. Consistent with this smaller size, the Al⁺ complex has the shortest M⁺-O bond distance of these three complexes. In light of its smaller size and closer approach to the carbonyl, it is then understandable that the polarization of the carbonyl is greatest for Al⁺. Interestingly, although the vibrational shift is greatest for Al⁺, this complex is apparently not the most strongly bound of the three. It appears then that the vibrational shifts and the dissociation energies of these complexes do not follow the same trend. We have found this same effect previously in a series of transition metal ion complexes with acetylene.¹²² Frenking and co-workers have decomposed the various contributions to metal-ligand bonding and have explained that vibrational shifts depends on the strength of the interaction but also on on the details of the M⁺-L separation and the specific orbital interactions involved in bonding.^{120, 121}

Figure 5.4 Infrared photodissociation spectra of Mg⁺(acetone)Ar with the carbonyl carbon substituted with the ¹³C isotope in the upper trace and natural abundance acetone in the lower trace. For the substituted complex, the shift of the doublet to lower frequencies and a shift in relative intensities are indicative of a Fermi resonance.





5.5 Conclusions

Metal cation complexes, M^+ (acetone)Ar (M = Mg, Al, Ca) are produced in a cold molecular beam environment and studied with infrared photodissociation spectroscopy in the carbonyl stretch region. These experiments are made possible by the availability of recent advances in technology allowing crystals to extend the tuning range of infrared OPO/OPA laser systems to longer wavelength region of the infrared spectrum. In addition to our IR-REPD experiments, the structures and spectra of these complexes are investigated with density functional theory. The spectroscopy and theory are consistent with structures having the metal cation binding on the oxygen of the carbonyl for all three complexes. The carbonyl stretch vibrations in each of these complexes shifts to lower frequency compared to its value in the free acetone molecule. This affect is attributed to a chargetransfer interaction because the metal cation withdraws bonding electron density from the carbonyl. The effect is greatest for the closed-shell aluminum cation because of its smaller size and greater charge density, which enhances its ability to induce polarization of the carbonyl electrons. A Fermi resonance between the carbonyl stretch and the overtone of the symmetric carbon stretch vibrations leads to a doublet structure at the carbonyl band for Mg⁺ and Ca⁺ complexes. However, this accidental degeneracy is not found for the Al⁺ complex because the carbonyl stretch occurs at much lower frequency relative to the overtone of the C-C-C symmetric stretch ($\sim 50 \text{ cm}^{-1}$). The qualitative trends in the carbonyl stretch vibrational frequencies do agree well with theory, but the absolute values of the vibrational frequencies are sensitive to the scaling factors employed. We find that the best overall agreement between theory and experiment in these simple model systems occurs when a vibrational scaling factor of 0.990 is employed.

These acetone complexes provide useful models for cation-carbonyl interactions similar to those that occur throughout chemistry and biology. Similar complexity from Fermi resonances for vibrations may occur in the region of the carbonyl stretch for many metal-organic systems. It is also likely that these same issues will arise in the amide I region of metal ion complexes with amino acids and peptides as higher quality spectra become available for these systems. Bench-top OPO/OPA systems provide significantly higher resolution than that available from FEL laser sources, making it possible to observe this structure and to probe these spectra in more detail. Likewise, the issues found here for vibrational scaling factors are likely to become relevant for the spectroscopy of many new metal ion molecular systems as work progresses in the lower frequency regions of the infrared. The singly charged metal ions studied here are clearly not in their most common charge states found in solution or in biology. However, the features of cation-carbonyl interactions revealed here, including the dependence on cation size and electronic structure rather than just binding energy, are expected to be central issues as more realistic systems are investigated.

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CHAPTER 6

CONCLUSIONS

We use laser vaporization coupled to a supersonic expansion to synthesize gas phase metalcontaining complexes for investigation. Due to the numerous controllable parameters, this method for complex production lends itself well as the method-of-choice for studying many different kinds of systems. The source can generate variable cluster species or metal-ligand complexes with variable size. Moreover, this technique has proven its efficacy at generating relatively cold complexes. Coupling this source to a modified reflectron time-of-flight mass spectrometer provides the capacity to study systems with infrared photodissociation spectroscopy. The action spectra generated provide a practical means for understanding structure, bonding and coordination numbers in metal-ligand complexes. In this work, our instrument has been used to study the differing interactions of metal carbonyl species in the gas phase.

Carbon monoxide is a unique molecule that often violates the paradigms in chemistry. Upon examination of the electronegativities of atoms, one might suppose that the O end is more negative in this diatomic. However, the opposite it true and the C terminus in the molecule bears the partial negative charge due to the atom's larger atomic orbital contribution to the resultant molecular orbital. Indeed, CO binds end-on through the carbon to a metal center. Such an end-on binding motif is observed for most metals and their ions. Carbon monoxide has a rich electron density which can be activated for use in many laboratory- and industrial-scale synthetic processes. This molecule can bind in a variety of ways to metal surfaces, as evidenced by vibrational spectra. And when CO becomes bound up as a carbonyl functional group in an organic molecule, it can greatly change the reactivity and geometry of that molecule. The carbonyl group is of fundamental importance even to life as an important constituent in the amide functional group of amino acids. Hence CO and organic carbonyl compounds form a class of molecules that have important implications in

fundamental synthesis work and catalysis as well as the characteristics of many other more biologically, economically and chemically important systems.

Many times these synthetic and catalytic pathways require the use of a metal center, metal cluster or metal surface to coordinate, activate or direct the reactant-to-product conversion. Hence, metal carbonyl species form an important component of traditional chemical compounds as well as the biochemical processes of life and much work has attempted to understand their chemical behavior. Interestingly, this class of inorganic complexes was one of the first to be synthesized, isolated and characterized in the laboratory, nearly 150 years ago. And the basic framework for their bonding, the Dewar-Chatt-Duncanson model, was proposed more than 50 years ago. Yet even today they remain as important species for study as techniques improve and technology develops new ways to probe their structure and chemistry. By and large, most metal carbonyl systems exhibit classical behavior, with significant metal backbonding, strong metal-ligand bonds, weak C-O bonds and decreased vibrational stretching frequencies. However, there are documented observations that nonclassical behavior is observed for certain metal carbonyl species in the gas phase generated with a laser vaporization/supersonic expansion source and probed with photodissociation action spectroscopy.

Specifically, the work presented here has examined the vibrational shifts of gas-phase metal carbonyl complexes relative to the free CO stretch. We provide the first evidence for such behavior in gas phase atomic gold cation carbonyl complexes, in collaboration with theorists. In $Pt^+(CO)_n$ complexes we have observed what we believe to be true a synergy in the two metal carbonyl bond-ing motifs that leaved the bound carbonyl stretching frequency almost unchanged from the free CO

stretch. This is evidenced by the very small shift observed in the vibrational spectra associated with the n = 4 complex. Finally, we have examined the carbonyl stretches in M⁺(acetone), M = Mg, Al and Ca, and in conjunction with density functional theory understood their vibrational shift. Interestingly, the acetone complexes with magnesium and calcium ions display a Fermi resonance, which was not anticipated initially. For all of these metal ion ligand systems, the magnitude and direction of the vibrational shifts give important clues as to the nature of the binding in these systems.

In a clearly nonclassical interaction, the Group 11 atomic gold cation shifts the stretching frequency of CO significantly to the blue by 60-70 cm⁻¹. This points to a largely electrostatic type interaction in which the dative bonding has little or no covalent character. Gold was chosen because as a reactive surface it has received much attention in the recent decade. This noble metal, so named because of it apparent inertness, has been found to lose its nobility and have high catalytic capacity when subjected to specific environments. Additionally, condensed phase reports of gold carbonyl species with counterions present have observed the blue shifts gold causes on carbonyl stretch frequencies. It is unfortunate that we were unable to obtain spectra for the n = 1 and 2 complexes even with Ar tagging, as these data would be able to provide a direct test of theory. The closed-shell nature of Au⁺ makes computational study more feasible so long as relativistic effects for the 5d ion are considered. New improvements in the ability to attach very weakly bound tagging molecules or atoms are underway with an modified and improved source design. Hopefully these improvements will pave the way for Ne-, or even He-tagged complexes, which should fragment upon irradiation with \sim 2150 cm⁻¹ or smaller photons. Furthermore it would be interesting to observe spectra for the other Group 11 noble metal atomic ions, Cu⁺ and Ag⁺ complexed with CO. These are expected to behave similarly to Au⁺, but experiments are necessary to determine this.

Unlike gold, platinum has long been known to be an effective reactive surface and is used widely in synthesis and catalysis. The mass spectrum of $Pt^{+}(CO)_{n}$ shows a marked enhancement in the intensity of the n = 4 complex. This enhancement can point to a coordination number for platinum cation of four. Additionally, the breakdown patterns show that the larger complexes fragment to the terminal ion n = 4. Consistent with this coordination number, the n = 5 and 6 IR spectra have peaks that fall on top of the n = 4 spectrum, which implies that these larger complexes have a 4+1 and 4+2 binding configurations, respectively. This suggests that the three spectra obtained are of the n = 4 complex with the fifth and sixth CO molecules binding in the second coordination sphere. In our IR study of gas-phase atomic platinum cations with CO ligands, a definition as being strictly classical or nonclassical is not so apparent. This open shell ion has an unpaired d electron which can contribute to the back bonding. This apparent back bonding largely offsets the blue shift resulting from the dative on-axis binding resulting in blue shifts near 10 cm⁻¹. No high level calculations for the platinum ion complexes are available as Pt⁺ has an open shell structure in addition to requiring a relativistic treatment. We can however point to a highly symmetric structure for the n =4 complex as evidenced by the single-peak spectrum. This finding is in agreement with previous work using mass spectrometric methods and density functional theory to measure the structure and binding energies of $Pt^+(CO)^n$, n = 1-4 complexes. Like the gold complexes, it would be convenient to be able to measure the smaller complexes, and hopefully improvements to our source will facilitate this.

While in the same vein as the cationic gold and platinum carbonyl studies, the metal acetone studies here are slightly different. This was the first application of tunable far-IR generated by the newly-available AgGaSe₂ crystal to study a metal-ligand complex in the gas-phase. This photodissociation study involved main group metals and the organic carbonyl acetone and calculations using

density functional theory. Main group metals such as Mg, Al and Ca have significant importance in biological systems, and this study was aimed at being a first step to understanding the binding of metals to the amide moiety of an amino acid. To study these main group metal-acetone interactions, we relied on the rare gas tagging technique, and the binding energies of Ar to Mg⁺, Al⁺ and Ca⁺ are such that efficient photodissociation was observed. Unlike transition metals, these main group metals can offer no d electrons for back bonding, so only an on-axis σ -type interaction is expected. Largely because of the binding motif (the metal binds to the O in the acetone carbonyl), significant red shifts are observed in the vibrational spectra. But the unexpected observation of a Fermi resonance for Mg⁺ and Ca⁺ complexes was determined to be from the accidental degeneracy of the first overtone of the C-C-C stretch and the C-O stretch with density functional theory. While not being quantitatively accurate in the magnitude of the shifts, DFT provided qualitative agreement with our observations. The magnitude of the shifts can be understood in light of the relative ionic radii for the three metals.

Determination of the structure, bonding and energetics in isolated complexes is a first step that can lead to developments in new synthetic and catalytic routes for organometallic chemistry, understanding and enhancement of biochemical systems and our ability to test and better develop theoretical models. Moreover, the path to chemical understanding results in improved insight and hopefully an overall better appreciation of the Universe. Finally, to paraphrase Feynman, there is pleasure in finding things out. Ultimately, the goal of any study is to provide added insight into the nature of things, and hopefully we have scratched the surface here.