

SPECTROSCOPIC STUDIES OF NON-COVALENT METAL ION-LIGAND INTERACTIONS

A Dissertation Presented

by

ABDULKADIR KOCAK

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Abdulkadir Kocak

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DEDICATION

To my lovely wife, Melek, and to my parents

*"İlim ilim bilmektir,
İlim kendin bilmektir,
Sen kendin bilmezsın,
Ya bu nice okumaktır"*

-Yunus Emre

ABSTRACT

SPECTROSCOPIC STUDIES OF NON-COVALENT METAL ION-LIGAND INTERACTIONS

MAY 2014

ABDULKADIR KOCAK, B.S., ONDOKUZ MAYIS UNIVERSITY

M.S., UNIVERSITY OF MASSACHUSETTS AMHERST

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Directed by: Professor Ricardo B. Metz

Non-covalent interactions between metal ions and ligands such as water and methane have been extensively studied due to their biological and industrial importance. Gas phase studies can reveal the fundamental nature of these metal-ligand interactions. Photofragment spectroscopy is a powerful technique to investigate bond strengths, dissociation dynamics, molecular geometry and clustering and can be applied to electronic and vibrational spectroscopy. Using a home built apparatus, which combines ion production via laser ablation, separation via time-of-flight (TOF) mass spectrometry, laser excitation, and TOF fragment mass analysis, we have obtained electronic spectra of $\text{Co}^+(\text{H}_2\text{O})$ and vibrational spectra of $\text{M}^+(\text{CH}_4)_n$ ($\text{M}=\text{Co}, \text{Ni}, \text{Cu}, \text{Ag}; n=1-4 \text{ or } 1-6$). The experimental techniques, apparatus, data acquisition and analysis employed throughout this thesis are described and explained in chapters 1 and 2.

Chapter 3 discusses the electronic spectra of $\text{Co}^+(\text{H}_2\text{O})$, $\text{Co}^+(\text{HOD})$ and $\text{Co}^+(\text{D}_2\text{O})$, measured from 13500 cm^{-1} to 18400 cm^{-1} using photodissociation spectroscopy. Transitions to four excited electronic states, with vibrational and partially resolved rotational structure are observed. The $\text{Co}^+-\text{(H}_2\text{O)}$ binding energy is determined from the dissociation onset. The

experiments and supporting calculations provide detailed information such as the electronic configuration of excited electronic states, how the Co^+ electronic state affects the $\text{Co}^+-\text{H}_2\text{O}$ bond strength, and how binding to Co^+ changes the geometry of water.

Chapter 4 discusses measurement and analysis of vibrational spectra of $\text{M}^+(\text{CH}_4)_m(\text{Ar})_{3-m}$ and $\text{M}^+(\text{CH}_4)_n$ ($\text{M}=\text{Co}, \text{Ni}$; $m=1,2$; $n=3,4$) in the C-H stretching region ($2500\text{-}3100\text{ cm}^{-1}$).

Interaction with the metal leads to large red shifts in the C-H stretches for proximate hydrogens.

The extent of this shift is sensitive to the methane coordination (η^2 vs. η^3) and to the metal-methane distance. The structures of the complexes are determined by comparing measured spectra with those calculated for candidate structures. All complexes show η^2 methane coordination and the d orbital occupancy determines which structures are preferred. Chapter 5 extends these studies to $\text{M}^+(\text{CH}_4)_n$ ($\text{M}=\text{Cu}, \text{Ag}$; $n=1\text{-}6$). Clusters have η^2 methane coordination and prefer symmetrical structures due to the d^{10} spherical electronic configuration of M^+ . Clusters with $n>4$ also show features from second shell ligands. Chapter 6 discusses extending this work to metal cluster ion -methane interactions.

ÖZET

KOVALENT OLMAYAN METAL İYONU-LİGAND ETKİLEŞİMİNİN SPEKTROSKOPİK ÇALIŞMALARI

ŞUBAT 2014

ABDULKADİR KOÇAK, LİSANS., ONDOKUZ MAYIS ÜNİVERSİTESİ

YÜKSEK LİSANS, UNIVERSITY OF MASSACHUSETTS AMHERST

DOKTORA, UNIVERSITY OF MASSACHUSETTS AMHERST

Danışman: Prof. Dr. Ricardo B. Metz

Metal iyonları ve ligand arasında kovalent olmayan kuvvetli etkileşimler biyolojik ve sanayisel olarak önemli olduğundan sıklıkla çalışılmıştır. Hem elektronik hem de vibrasyonel spektroskopi olarak uygulanabilen gaz fazda foto-parçalama spektroskopisi bağ kuvvetleri, parçalanma dinamiği, molekül yapısı ve kümelenmesi gibi konularda bilgi edinmemizi sağlar. Lazerle iyon üretme, uçuş sürelerine göre kütle analizi (TOF-MS), lazerle foto-uyarma, ve foto-fragman analizinin kombine edildiği cihazımızın detayları ve uygulanan farklı metodlar 1. ve 2. bölümlerde tartışılmıştır.

3. bölümde $\text{Co}^+(\text{H}_2\text{O})$, $\text{Co}^+(\text{HOD})$ ve $\text{Co}^+(\text{D}_2\text{O})$ 'nin 13500 cm^{-1} 'den 18400 cm^{-1} 'e kadar ölçülerek vibrasyonel ve rotasyonel yapılarını aydınlattığımız 4 farklı elektronik geçiş hali (foto-uyarılmış hal) ve $\text{Co}^+(\text{H}_2\text{O})$ bağ enerjisi tespit edilmiştir. Deneyler ve teorik hesaplamalar sayesinde uyarılmış hallerin elektronik konfigürasyonu, Co^+ iyonlarının Co-O bağ enerjisini ve suyun yapısını nasıl etkilediği tartışılmıştır.

4. bölüm $\text{M}^+(\text{CH}_4)_m(\text{Ar})_{3-m}$ ve $\text{M}^+(\text{CH}_4)_n$ ($\text{M}=\text{Co}, \text{Ni}$; $m=1,2$; $n=3,4$) iyonlarının $2500\text{-}3100\text{ cm}^{-1}$ 'de vibrasyonel spektrumlarını içermektedir. Metanların metal iyonlarına olan bağlanma

enerjisi ve koordinasyonu metal iyonlarının doğasına, elektronik konfigürasyonuna ve büyüklüğüne bağlı olarak değiştiği; deneysel ve teorik hesaplamalarla hangi yapıların oluştuğu tespit edilmiştir. Genellikle güçlü etkileşime sahip olan bu iyonlarda hidjojenlerin iki tanesinin koordine olduğu (η^2) ve bunda da metal iyonlarının 4s orbitallerinin boş olması ve tam dolu olmayan d orbitallerinin etkisinin büyük rol oynadığı tespit edilmiştir. 5. bölümde bu çalışmalar $M^+(CH_4)_n$ (M=Cu, Ag; n=1-6) iyonlarını da içerecek şekilde genişletilmiştir. Cu^+ ve Ag^+ iyonlarının d orbitalleri tam dolu olduğu için bunlara ait komplekslerin genellikle daha çok simetrik olan yapıları tercih ettiği anlaşılmıştır. Ayrıca n>4 olan komplekslerde ilave metan ligandlarının birinci koordinasyon tabakasında olmadığı tespit edilmiştir.

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I would like to express my deepest gratitude to all the people around me, who created an exceptional environment, which made me who I am. And I would like to ask for their blessings and forgiveness for anything I did wrong intentionally and unintentionally.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

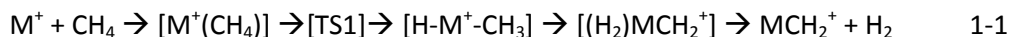
Transition metals catalyze a wide range of reactions, from the hydrocarbon transformations that produce next generation fuels to the enzymes essential for life. Understanding the mechanisms of these reactions has been a long-standing goal of scientists. The key to these reactions is the microscopic covalent and non-covalent interactions between the metal, the substrate and solvent/ligand environment. Non-covalent interactions such as ion–dipole and ion-induced dipole can be surprisingly strong, approaching the strength of covalent bonds. Gas phase studies reveal the core nature of the metal-ligand interactions, avoiding complications from neighboring molecules that are present in the condensed phase. In this work we explore non-covalent interactions of transition metal ions with water and methane.

1.2 Motivation

The importance of metal ion-water interactions in solvation, catalysis and biology has inspired numerous experimental and computational investigations of metal ion-water complexes. Gas-phase studies allow for detailed examination of ion-solvent interactions, including their dependence on the ions' charge and electron configuration and the number of solvent molecules. Studies have also examined how interaction with the ion affects the solvent molecules.¹ In addition to measurements of metal-water binding energies using equilibrium methods,² bimolecular reactions,³ and collision induced dissociation,⁴⁻⁶ vibrational and electronic spectroscopy can reveal structure and bonding in the complexes.

Methane is a permanent gas, which makes it awkward to transport and store and precludes its use as a fuel for vehicles. Thus, direct, efficient conversion of methane to a liquid such as larger hydrocarbons or methanol has been a long-standing goal of catalysis.⁷

Activation of methane by gas phase metal ions



is exothermic and occurs under thermal conditions for most third-row transition metals while it is endothermic for the first and second-row metals.⁸⁻¹¹ Gas phase metal cations are thus an excellent model system as they have the desired reactivity and can be studied in detail by experiment and theory. This has prompted numerous studies of methane activation by gas-phase metal atoms and ions.^{10,12-18} The first step in this reaction is formation of an $M^+(CH_4)$ entrance channel complex. In addition, some metals show cooperative effects in reacting with methane, binding to two CH_4 before C-H activation occurs.¹⁹

The M^+-CH_4 interaction involves varying extent of covalency, depending on the metal. The same techniques which have been used to characterize $M^+(H_2O)$ complexes have also been applied, but less extensively, to $M^+(CH_4)$. Vibrational spectroscopy is especially useful in characterizing the methane complexes, as the C-H stretching frequencies are very sensitive to the structure and M^+-C bonding / C-H antibonding interactions.

1.3 Absorption vs. Photodissociation Spectroscopy

Electronic and vibrational spectroscopy is a great tool to investigate the physical properties of matter and can be carried out in two basic ways. The light-matter interaction event can be monitored directly via “Absorption Spectroscopy” or resulting events can be monitored via “Consequence Spectroscopy”. Absorption spectroscopy deals with the light absorbed by a sample (Beer-Lambert Law), and it is an ideal tool to study bulk systems or gas

phase molecules at fairly high concentration. However, it is not sensitive enough to apply to very low concentrations of molecules, such as gas-phase metal ion-ligand complexes. Consequence spectroscopy detects changes in the molecule after light is absorbed, for example by monitoring fluorescence or dissociation. In contrast to absorption spectroscopy, which detects a reduction in a large quantity (the incident light), consequence spectroscopy measures the increase in a small quantity. It is thus a nearly zero background technique and can be used to measure spectra of dilute, weakly absorbing systems. We use photodissociation consequence spectroscopy to study the electronic and vibrational spectra of gas-phase ions. This is an ideal technique to use with gas phase ions because the fragment ions have a different mass from the parent and thus they can be easily distinguished from the parent ions using the mass spectrometer. The implementation and application of this technique will be discussed in Chapter 2.

The dissociation can occur in two ways: directly or indirectly. In a direct dissociation the molecule is excited to a repulsive potential and dissociates rapidly. This leads to a broad, typically unstructured spectrum, giving very limited information. In an indirect dissociation (Figure 1.1), the excited state has a minimum, and thus bound vibrational states. Absorption occurs to various vibrational levels in the excited states. In order for dissociation to occur, the energy in the initially excited state has to transfer to a dissociative state, from which the molecule dissociates. This process occurs via internal conversion or intersystem crossing.²⁰ There are two limiting time frames for the excited state, If the excited state lives less than 0.1 ps, the resulting Lorentzian linewidth is greater than 50 cm^{-1} and so there is very little structure in the spectrum. If the excited state lives too long ($>100\text{ ns}$ - $5\text{ }\mu\text{s}$), then the dissociation yield is very small either due to the competition with fluorescence (occurs in 5 ns - $5\text{ }\mu\text{s}$, depending on the molecule) or because the molecule falls apart outside the window that our time-of-flight

(TOF) mass spectrometer can separate the fragment and parent ions ($>5 \mu\text{s}$). Within these limits, the photodissociation spectrum is very informative and contains vibrational and even rotational structures. This is the case in the electronic spectroscopy of $\text{Co}^+(\text{H}_2\text{O})$, which will be discussed in Chapter 3.

This dissertation is organized in the following manner. Chapter 1 introduces the systems of interest and the technique used to characterize them. Chapter 2 describes the experimental apparatus and various techniques used to measure electronic and vibrational spectra. Chapter 3 discusses the results of electronic spectroscopy and vibrationally mediated photodissociation spectroscopy of $\text{Co}^+(\text{H}_2\text{O})$ and its isotopomers. In this chapter, we investigate the $\text{M}^+(\text{H}_2\text{O})$ binding energy and effect of metal ion on water structure and effect of the electronic configuration of the metal ion on the $\text{Co}^+ - \text{OH}_2$ bond strength. In chapter 4, we investigate metal ion – methane complexes for Co^+ and Ni^+ via vibrational spectroscopy. By comparing measured spectra to spectra calculated for potential structures, we identify the ground state structures for $\text{Co}^+(\text{CH}_4)_{1-4}$ and $\text{Ni}^+(\text{CH}_4)_{1-4}$. In chapter 5, we extended these studies to Cu^+ and Ag^+ in order to explore periodic trends across the transition metals including open shell vs. closed shell, and smaller vs. larger metals. In chapter 6, we describe extensions to other interesting systems.

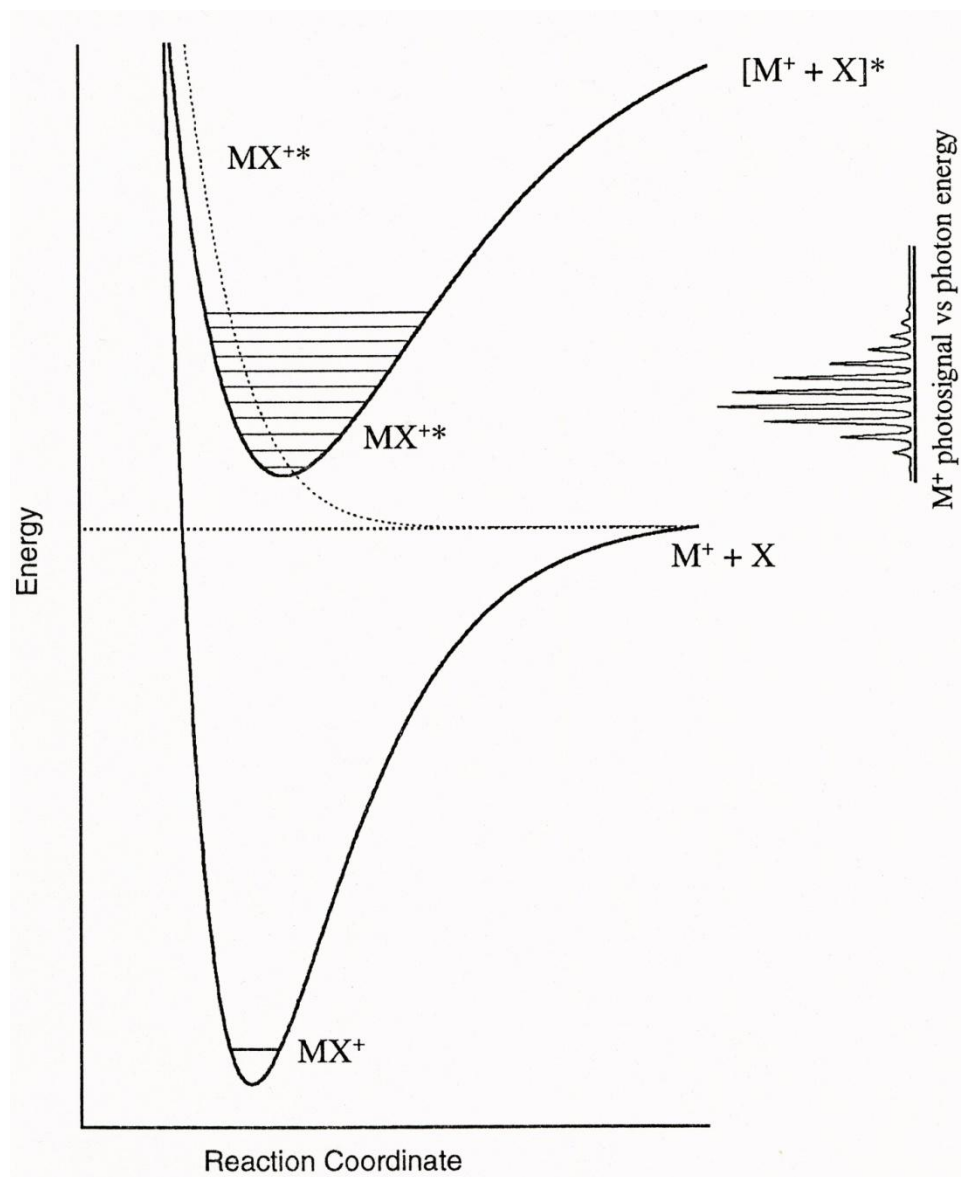


Figure 1.1 An illustration of the photofragmentation process. The consequence of absorption of a photon is dissociation of the ion.

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CHAPTER 2 EXPERIMENTAL

2.1 Apparatus Overview and Parts

The studies described in this thesis were carried out using a Laser Ablation Source Dual Time-of-Flight Reflectron Mass Spectrometer (shown in Figure 2.1), which is also described in detail elsewhere.¹ Briefly, parent ions are produced in the source chamber by reacting M^+ , produced by ablating a metal rod, with a neutral reactant gas. Ions are cooled, accelerated, mass selected, and photodissociated at the reflectron turning point by a second laser, which can be an IR OPO/OPA or a visible dye laser, and finally parent and photofragment ions are detected and distinguished by their flight times. The parts of the instrument will now be described in detail; letters refer to Figure 2.1.

A: Ablation Laser. Either a Minilite (Continuum) or Surelite (Continuum) Nd:YAG laser is used. The 1064 nm output is doubled to produce 15mJ/pulse at 532 nm, which is focused with a 1m lens to a 0.15 mm dia. spot on the metal surface. In principle, increasing the power of the ablation laser will provide more metal ions. However, there is a limiting factor to this. Since the ablation laser hits the metal rod after the precursor is introduced, higher powers result in decomposition of the precursor molecules in the intense plasma formed by the ablation laser. This leads to a very noisy, congested mass spectrum.

B: Metal rod. In order to ablate a fresh portion of the rod on each shot, the rod is rotated (at ~2 min/rev) and translated (1/80"/rev). So, a rod with 2" length can be run for 7 hours before the same spot is reached twice. Depending on the metal and precursor gas, the same spot can be run several times before the rod needs to be repolished. The metal rods are typically 0.250" dia. and >99.99% highly pure metals.

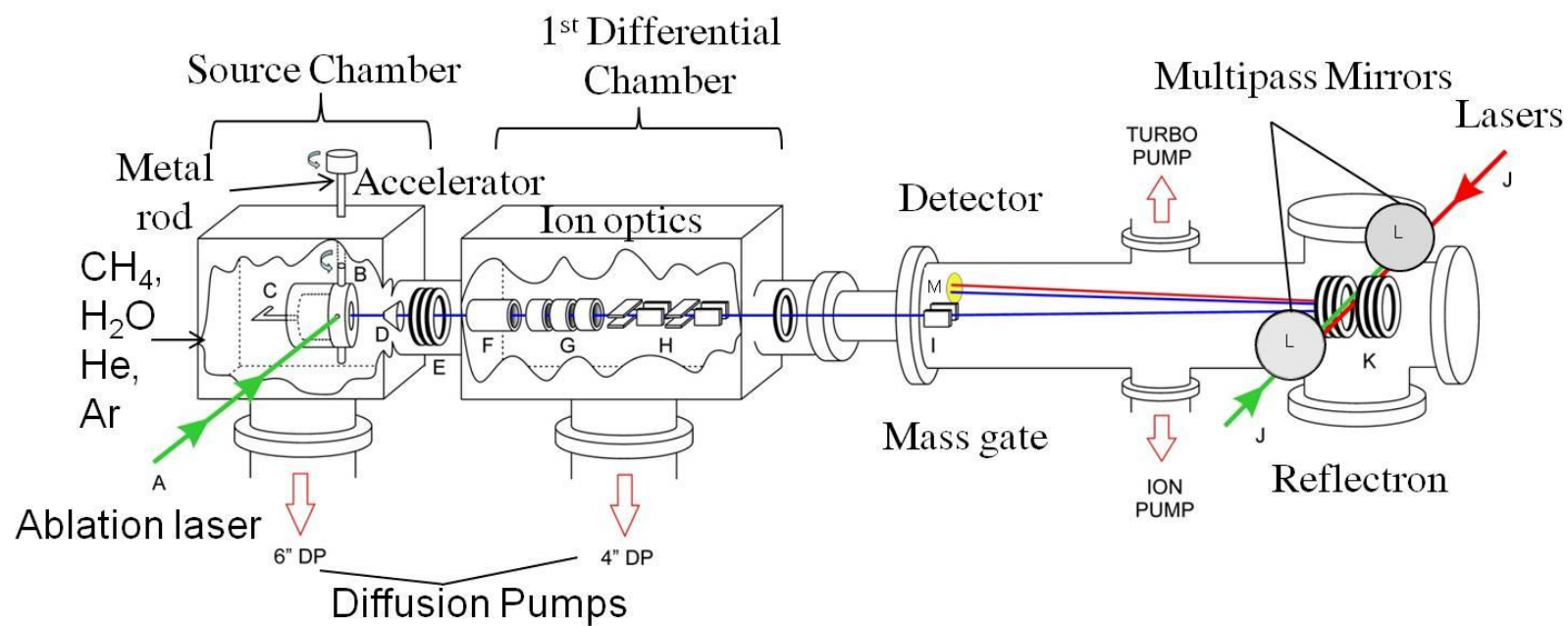


Figure 2.1 Schematic View of Dual Time-Of-Flight Reflectron Mass Spectrometer. Labels are explained in the text

C: Precursor gas. The $M^+(CH_4)_n$ and $M^+(H_2O)$ complexes are formed by clustering the ligand onto M^+ produced by laser ablation. A pulsed valve (piezo-electric valve or a General valve) introduces the precursor gas into the source chamber at a backing pressure of 1-5 atm. In these studies, the precursor (H_2O and CH_4) is diluted to <5% in helium or argon bath gas. Collisions with the bath gas cools the ions to ~ 300 K, then supersonic expansion into vacuum ($\sim 10^{-4}$ - 10^{-6} torr) further cools ions to rotational temperatures of ~ 15 K.¹⁻⁴

D: Skimmer. The molecular beam formed in the source passes through a 3 mm dia. skimmer to the first differential chamber

E: Acceleration region. Ions are accelerated in two stages (Wiley-McLaren⁵ type accelerator) to a potential of -1800V, and gain an equal amount of kinetic energy. Since $KE = 1/2 mV^2$, different masses will have different velocities, so they can now be separated according to m/z .

F: Re-referencing tube. To avoid floating the flight tube at -1800V, ions are re-referenced⁶ to ground potential. When they enter this 10 cm long, 5 cm dia. tube, the potential is -1800 V, before they exit it is rapidly pulsed to ground, so their kinetic energy is not changed, but now they are at ground potential.

G: Einzel Lens. On leaving the re-referencing tube, ions are cylindrically focused by this lens.

H: Deflectors. A set of vertical deflectors sandwiched by two sets of horizontal deflectors is used to focus and guide the ions into the detector chamber. Each deflector is a pair of plates, one of which is grounded and a small voltage (<15 V) can be applied to the other plate.

I: Mass gate. It is a final deflector for ions to traverse the reflectron and hit the detector through an angle of $\sim 5^\circ$. This deflector works with a constant or pulsed voltage of 30-60V. If the voltage is constant all the ions make it through to the detector. If it is pulsed, only those ions in

the deflector during the pulse will reach the detector. Depending on the width of the pulse, only ions within ~ 2 amu of the target mass are transmitted.

J: Reflectron. Entering ions are decelerated in an electric field, so they come to rest for a moment at the point where the potential in the reflectron is equal to their initial kinetic energy. Ions are dissociated at the turning point of the reflectron. The ions of a particular mass can be dissociated over a ~ 100 ns laser firing time window. The ions are then re-accelerated such that they exit with exactly the same kinetic energy as when they entered. This reacceleration means that fragment ions have different velocities and flight times than the parents.

K: Dissociation Laser. Ions of interest are photodissociated at the turning point of the reflectron by a pulsed laser (ns pulse length). Different dissociation lasers and techniques will be discussed later.

L: Multipass Mirror. In order to improve the photodissociation yield we use a Perry-type⁷ multi pass mirror setup. This consists of two concave spherical, silver coated mirrors, bracketing the reflectron plates. Alignment using a HeNe laser shows that the laser makes 21 passes through the ion beam. Silver is used for its high reflectivity in the IR. However, it does not reflect in the UV, and dye laser must be attenuated to ~ 10 mJ/pulse to avoid burning the mirror.

M: Detector. The detector consists of two 40 mm dia. microchannel plates (MCP) and a solid stainless anode. When a charged particle strikes the surface near the entrance of a channel, electrons are ejected. A bias voltage accelerates these electrons, which strike the sides of the channel, ejecting more electrons. The MCPs have a net gain of 10^6 . This current pulse is converted to a voltage pulse using a 50 ohm resistor and is amplified 10 times to give a 2 ns wide, 20 mV pulse for each ion.

2.1.1 Ion Production

Two types of pulsed valves were used, and source conditions were optimized to maximize yield of the ions of interest.

2.1.1.1 Piezo-Electric Valve

The piezoelectric valve is adapted from a design by Proch and Trickl.⁸ The typical pulse widths range from 170 to 250 μs with $\sim 50 \mu\text{s}$ rising/falling times. A ceramic piezoelectric disk holds a plunger, on which a Viton o-ring tipped poppet is attached. This poppet normally seals a 0.5 mm orifice. To open the valve, high negative voltages (0 to -1000 V) are applied to the disc, causing it to flex, the plunger and o-ring to pull back and allowing the gas to flow. The width is generally kept constant and high voltage is tuned to open the valve. It produces very consistent, stable pulses and does not leak. However, it behaves erratically above 3 atm.

2.1.1.2 General Valve

The General valve, now called Parker Series 9, consists of a coil assembly, a ferrite-armature holding a Teflon or Kel-F poppet and a front plate with an orifice of 0.5 mm. A voltage is applied to the coil produces on magnetic field, which pulls the magnetic armature back, allowing gas to flow through the orifice. It is designed to operate at 24 V with 5ms opening time. By applying 300 V for $\sim 300 \mu\text{s}$ the valve opens for $\sim 250 \mu\text{s}$. In the General valve, the voltage is kept constant while the width is changed to increase the gas flow.

Although both of the valves are used for the same purpose, there are slight differences in details. To make small clusters, very low backing pressures are used and piezoelectric valve becomes more advantageous due to its stability at low pressures. For these cases, a typical precursor concentration of <1-2% and pressures of <3 atm. forms ideal source conditions. On

the other hand, the General valve becomes a good alternative for making larger clusters, which require high backing pressures and more concentrated gas mixtures. In general, the piezoelectric valve tends to give cooler ions at lower concentrations of bath gas. However, we could get colder ions with the General valve using higher concentrations of precursor and high backing pressure. Production of argon-tagged ions requires the highest backing pressures (up to 6 atm.), requiring the use of the General valve. Different precursors and coolant gases will be discussed in the corresponding chapters.

2.1.2 Laser Systems

Lasers are used for ion production (ablation) and for photodissociation spectroscopy. These are all fixed wavelength Nd:YAG lasers, or are tunable lasers that are pumped by a Nd:YAG. The lasers that are used for the experiments include a Continuum Minilite I (for ablation), Continuum Surelite I (for ablation and as a pump laser for a ND6000 dye laser), Continuum Powerlite 8020 and SpectraPhysics QuantaRay Lab Series 190 (as pump lasers for a Laservision IR OPO/OPA system).

2.1.2.1 Nd:YAG Lasers

As an ablation laser, in early experiments, we used a Continuum Minilite I Nd:YAG laser operating at a repetition rate of 20 Hz. Its 1064 output is frequency doubled to give ~10-15 mJ/pulse at 532 nm with a pulse width of 5-7 ns and a linewidth of 1 cm^{-1} . Later, as ablation laser, we have used a Continuum Surelite I-20, also an internally Q-switched Nd:YAG. The same laser was used as a pump laser for the ND6000 dye laser in previous studies by externally Q-switching. The Surelite I produces ~100-135 mJ at 532 nm at a rep. rate of 20 Hz with 4-6 ns pulse width. This power is directly used as pump power for the dye laser at 532 nm, but is reduced by ~90% via a beam splitter for ablation to provide 10-16 mJ of power. To pump the IR

OPO/OPA system, we used a Powerlite 8020, externally Q-switched, attenuated to ~500-550 mJ/pulse at 1064 nm with 20 Hz rep. rate. The linewidth is 0.7 cm^{-1} . A SpectraPhysics QuantaRay is used for pumping the IR OPO/OPA system in the later experiments. It has ~900 mJ at 1064 nm with 10 Hz rep. rate. With an attenuator, the power is reduced to 550-700 mJ/pulse before entering the IR OPO/OPA system in order not to damage the IR crystals. We updated to using this laser because it has a much more uniform beam than the Powerlite.

2.1.2.2 ND6000 Dye Laser

The electronic spectroscopy studies use a ND6000 dye laser for photodissociation. The core of the ND6000 dye laser is a dye oscillator and two dye amplifier cells, all of which are designed to be pumped by an external Continuum Powerlite or Surelite series ND-YAG laser. In our early experiments, we pumped with a Surelite whereas later we pumped with Powerlite (described above). Thus, the input pump energy for the dye laser becomes 130-300 mJ at 532 nm. A dye solution is circulated to absorb the beam at 532 nm and emit (fluorescence) at higher wavelengths. The wavelength is selected by tuning the angle between the grating and a mirror in the oscillator cavity. The beam power is amplified through two amplifiers. The power output is typically 10-25% of the pump power. Although the output can be doubled to work in the UV region, our experiments only use the fundamental VIS wavelength ranges (543 nm to 740 nm). The laser line width is $<0.1\text{ cm}^{-1}$ (typically 0.05 cm^{-1}) for the dye fundamental and $<0.2\text{ cm}^{-1}$ for the frequency-doubled output.

An external computer controls the grating mirror angle to tune the wavelength. The wavelength of the fundamental output of the laser is calibrated using the photo-acoustic spectrum of water overtones or atomic absorption lines of neon using a neon cathode tube.

2.1.2.3 Laservision IR OPO/OPA

The Laservision IR OPO/OPA is a tunable IR laser system which produces 2 mJ/pulse at 2500 cm^{-1} and 15 mJ/pulse at 4000 cm^{-1} . This laser also uses an external Nd:YAG pump laser, requiring ~550 mJ at 1064 nm with ~6 ns pulse width. The pump beam is first split in two by a beam splitter, and one part is frequency doubled by a KTP crystal to produce 532 nm light. This pumps an Optical Parametric Oscillator (OPO) which uses nonlinear KTP crystals. In a second order non-linear crystal, if a beam with a frequency of ω_p enters the crystal, two output beams (signal and idler) exit the crystal with frequencies of ω_s and ω_i . The sum of the output waves' frequency is equal to the input wave's frequency. In our OPO, a pair of KTP crystals is placed in a lasing cavity formed by two end mirrors to improve the efficiency. The beam is also coupled with a grating to improve the efficient conversion to signal and idler. By changing the angle of the crystals, the signal/idler ratio can be varied. Thus, the beam in the OPO is divided into a visible signal beam (tunable from 712 nm to 880 nm; i.e. 11364 cm^{-1} to 14085 cm^{-1}) and a complementary near-IR idler beam (tunable from 2.1 to 1.35 microns; i.e. 7433 to 4712 cm^{-1}). In the Optical Parametric Amplifier (OPA) stage, four KTA crystals (two pairs) combine the idler of the OPO with the remainder of the split 1064 nm (9398 cm^{-1}) beam to produce mid-IR light at 2200 (1 mJ/pulse) to > 4000 cm^{-1} (15 mJ/pulse) using difference frequency generation. Typically, we produce. At the lower wavenumber values, the KTA crystals start absorbing. The IR linewidth is typically ~1.8 cm^{-1} .

A computer controls the angles of all six crystals using a servo motor (motor #2 – motor #7). There is also one servo motor for controlling the grating-mirror angle, which determines the wavelength (motor #1). This motor acts as the master to initiate the other motors' movements. It is critical to calibrate this motor so that we can make sure that what the computer thinks is 1 cm^{-1} movement is really 1 cm^{-1} . The calibration is made using N_2O , CH_4 , and H_2O IR absorption

spectroscopy described below. At each wavelength, all the crystals need to be positioned correctly to maximize the output power. This is done using a calibration curve in which the optimum motor position is fit to a polynomial as a function of wavelength. (Position = $C_0 + C_1(\lambda - L_0) + C_2(\lambda - L_0)^2 + C_3(\lambda - L_0)^3 + \dots$ up to 10th order is possible). The calibration curves provided by the vendor only allowed scans over a range of $\sim 100 \text{ cm}^{-1}$ before the power dropped excessively (by $\sim 50\%$). This is quite annoying, as O-H region scans cover a range of $\sim 300 \text{ cm}^{-1}$, and C-H region scans are even broader, 600 cm^{-1} wide. Smaller scans require re-optimizing the power in each region and concatenating files, some of which were measured at different power levels. Therefore, new calibration curves for the crystals needed to be determined. In order to do this, the optimum motor positions are determined at each wavelength by maximizing the power. Since the power does not die all of a sudden for small wavelength changes, the power tweaks can be made every $\sim 40 \text{ cm}^{-1}$. The resulting motor positions vs. wavelength values are fit to a polynomial. Ideally, the motor positions can be calibrated in a way that the wavelength scans will cover the whole IR region ($2500\text{-}4000 \text{ cm}^{-1}$) without recalibrating. Unfortunately, even using the highest order polynomial curve, it loses power in long range scans. We can overcome this problem by dividing the power scans into more than one region and use different calibration curves for different regions. Vibrational frequencies of O-H symmetric and antisymmetric stretches lie from ~ 3500 to 3800 cm^{-1} . Thus, for $M^+(\text{H}_2\text{O})$ studies, we can calibrate motor positions for only a 300 cm^{-1} range (from 3500 cm^{-1} to 3800 cm^{-1}). Similarly, the symmetric and antisymmetric C-H stretching frequencies for $M^+(\text{CH}_4)_n$ complexes lie from $\sim 2500 \text{ cm}^{-1}$ to 3100 cm^{-1} . Therefore, we only need a calibration curve that works in this range. Now we have two sets of calibration factors that will work in the two different regions.

In general the higher order polynomial, the better fit to the motor positions. On the other hand, if the calibration curve uses a smaller order polynomial, it will likely maintain power

even outside the calibration range it is calibrated whereas the higher order polynomials lose power rapidly once outside the range. For this reason we have used the lowest order polynomial possible (third order or less).

The wavenumber calibration is made using the rotationally resolved IR absorption spectrum of H₂O vapor in the 3100-3800 cm⁻¹ region, CH₄ gas in the 2600 -3200 cm⁻¹ region and N₂O gas from 2300 to 2600 cm⁻¹. Known spectra of these molecules are available from the high-resolution transmission molecular absorption database (HITRAN).^{9,10}

To obtain absorption spectrum we use a glass cell with sapphire entrance and exit windows. The cell is filled with the desired gas (N₂O, CH₄, or H₂O) at 0.025 to 1 atm. pressure and a power meter is placed after the exit window of the cell. When the IR is tuned to an absorption line, the power reading will be less. Since the P, Q, and R branches are obvious and very sharp (lines), it is straightforward to calibrate the laser wavelength (see Figure 2.2)

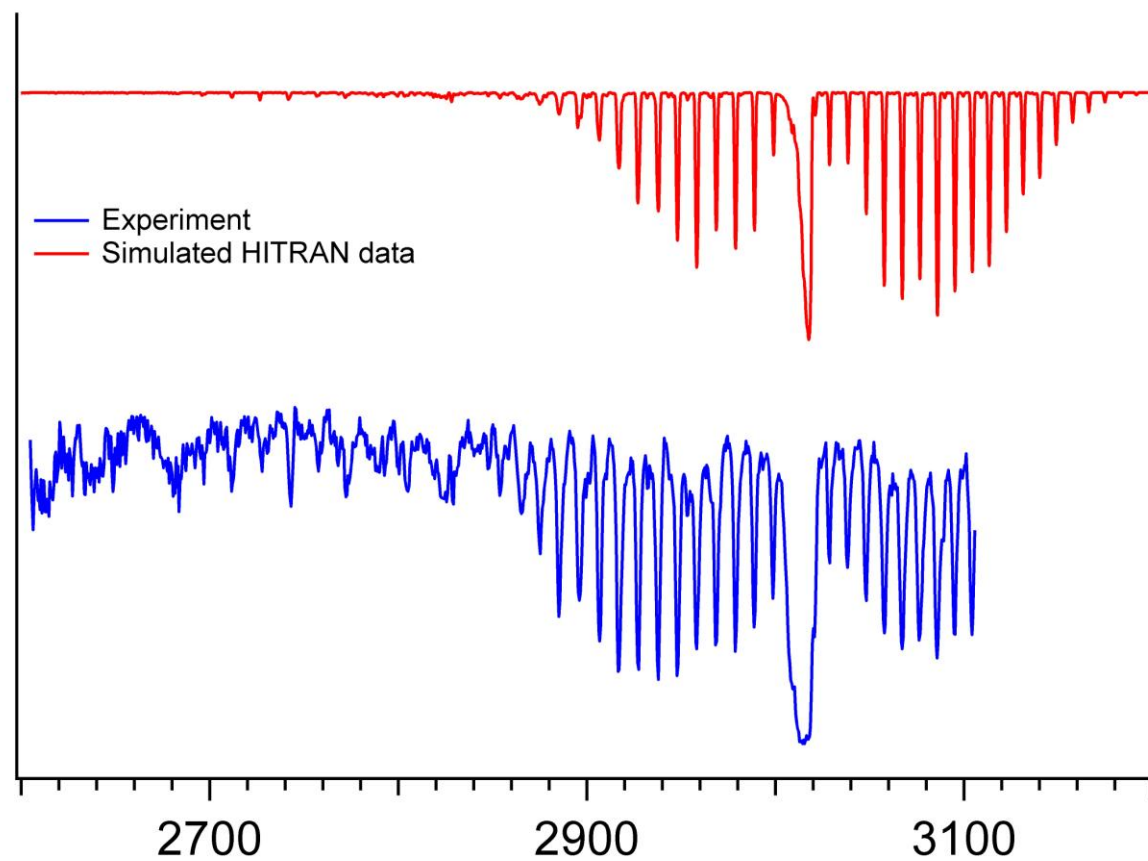


Figure 2.2 Experimental (blue) and simulated HITRAN (red) absorption spectra of CH₄. The experimental spectrum is shifted by +1.85 cm⁻¹ to match the HITRAN data. The Q branch line at 3016 cm⁻¹ is saturated.

2.1.3 Time of Flight and Timing

Timing for the pulsed photodissociation experiments is highly important. The ion production, selection and photolysis all involve voltage or light pulses. The relative times must be adjusted on a microsecond or sub-microsecond time scale. Initially, the pulsed valve (General or piezoelectric) is triggered at $t=0$. After that, the ablation laser flash lamp, extraction, re-referencing, mass selection, and dissociation laser flash lamp and Q-switch all need to be triggered in turn. A pair of DG 535 digital delay generators from Stanford Research Systems controls the timing. Each generator is able to generate four different time pulses. Some pulses (e.g. Data Valid) need to be extra long. Rather than using two channels to set the start and end time, a simple external one-shot circuit takes the pulse from the DG 535 and produces a 7 ms wide output pulse.

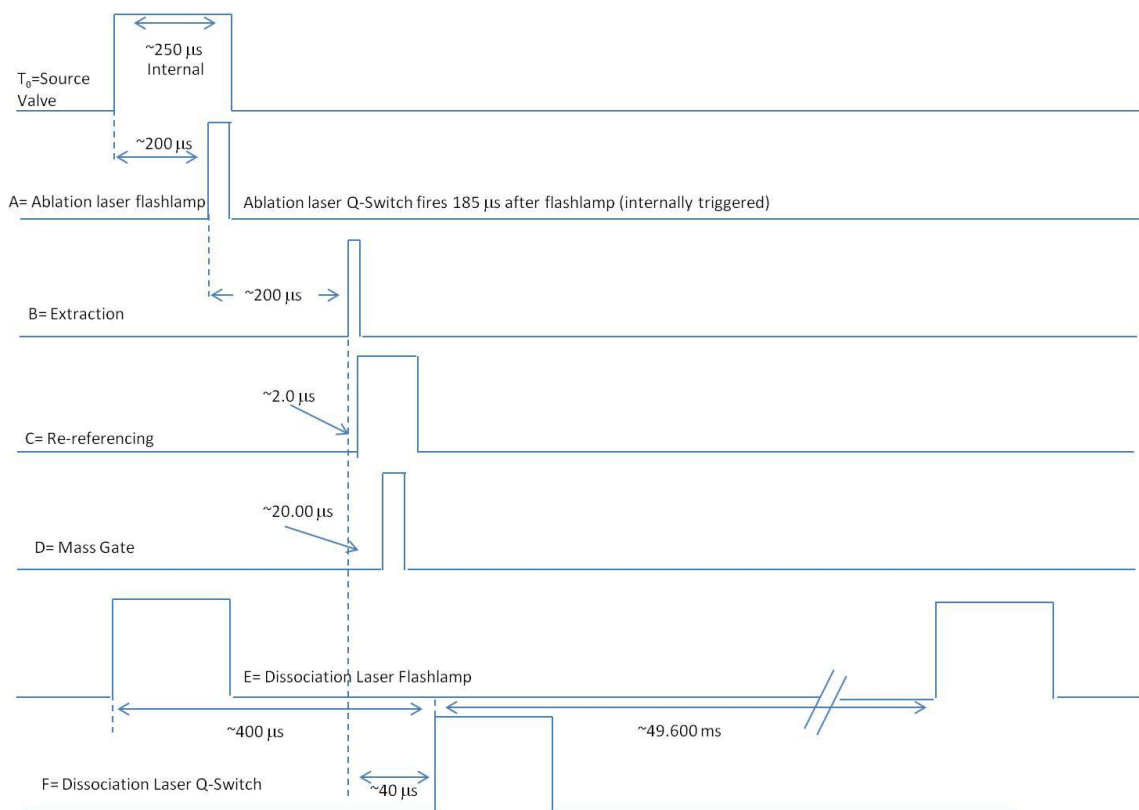


Figure 2.3 Time Delay Flowchart. The repetition rate is 20 Hz. This cycle repeats every 50 ms.

Figure 2.3 shows typical times for triggering different stages. First, the delay generator triggers the pulsed valve (at $t=T_0$). It takes time for the valve to physically open and for gas to flow to the rod. The flashlamps on the ablation laser fire after a $\sim 200\ \mu\text{s}$ delay; the Q-switch delay time is set internally to $185\ \mu\text{s}$ (and light comes out $<0.1\ \mu\text{s}$ later). The ablation laser time is adjusted to optimize the yield of the cold ions. The ions are extracted after a $\sim 200\text{--}250\ \mu\text{s}$ delay, depending on cluster size. The re-referencing pulse is $\sim 2.0\text{--}4.5\ \mu\text{s}$ after the extraction. The shorter times will allow only lighter ions to make it through while longer times will select only heavier ions. And finally, ions are mass selected with the pulsed mass gate, at typical delays of $15.00\text{--}25.00\ \mu\text{s}$ (according to the mass of the desired ions) with respect to extraction time.

By adjusting the timings mentioned above, parent ions can be successfully chosen. For the photo fragments, photodissociation laser timings also need to be adjusted. For the photodissociation lasers (both dye laser and IR laser), the flashlamp firing time and external Q-switch delay time are controlled by a second digital delay generator which is triggered from the first generator. For these lasers, the Q-switch time is triggered to overlap with the ions of interest. This is typically 20.00 to $50.00\ \mu\text{s}$ after the extraction, depending on the mass of the ion. The flashlamp-Q switch delay is kept constant for best power and beam quality, and is about $400\ \mu\text{s}$. Thus, the flashlamp fires $\sim 350\ \mu\text{s}$ before the extraction and, depending on the ion, might fire before the pulsed valve. The digital delay generator cannot apply negative time delays. We can solve this problem by using the fact that the experiment runs at exactly $20\ \text{Hz}$ repetition rate, controlled by the digital delay generator. So, each cycle repeats after exactly $50\ \text{ms}$ (with better than $1\ \text{ns}$ precision). So, a delay of $-400\ \mu\text{s}$ is equivalent to $+49,600\ \mu\text{s}$ ($49.6\ \text{ms}$).

The Nd:YAG pumped dye laser and the Powerlite 8020 used to pump the IR OPO/OPA in early experiments operated at $20\ \text{Hz}$. More recent experiments use the SpectraPhysics QuantaRay GCR 190-10, which operates at $10\ \text{Hz}$. So, IR data should be collected at $10\ \text{Hz}$,

synchronously with the firing of the IR laser. This is done by building an additional box that takes one pulse from the digital delay generator and sends it to trigger the YAG. Simultaneously, it generates a long blanking pulse. Any trigger pulses received during the blank pulse are skipped. That reduces the number of pulses by ½.

For time of flight and for singly charged ions:

$$KE = \frac{1}{2}mv^2 \quad 2-1$$

Since $v = \frac{L}{\tau}$, where L is the length of the flight tube and τ is the flight time,

$$\tau = \sqrt{\frac{L^2}{2}} \sqrt{m} \quad 2-2$$

We use the more precise relation:

$$\tau = c\sqrt{m} + t_0 \quad 2-3$$

where c (proportionality) and t_0 (a small time correction) are constants and m is the mass of the desired ion. Once we produce M^+ ions (whose mass we know), we first assume $t_0 = 0$ and find a rough c value (which is $\sim 5.88 \mu\text{s.amu}^{-1/2}$). Then we predict a second ion and find real t_0 and c values. After that, we apply this equation to find all the ions that we produce. If the metal has isotopes, we can get the constant values directly. The precision of the constants can be further improved by graphing the known masses and predicted times for ions that span a range of masses. The re-referencing time, mass gate time, and photolysis laser firing time all depend on mass of the ion. Once timing for one ion is found, the timing for the second ion can be calculated. Using equation 2-2 (with $t_0=0$),

$$t_2 = t_1 \sqrt{m_2/m_1} \quad 2-4$$

Thus, it is easy to switch between the ions of interest by changing the related times.

The parent ions' flight times will be different than those of the photofragment ions. The parent ions fly to the reflectron, decelerate, are irradiated, and parent and fragment ions re-accelerate and fly to the detector.

Their total flight time is

$$\tau_f = a\sqrt{m_p} + b\sqrt{m_f} + t_0 \quad 2-5$$

where m_p and m_f are the masses of parent and fragment ions. This equation also applies to undissociated parent ions, using $m_p = m_f$, and $a + b = c$. Subtracting equation 2-5 from equation 2-3, we can find the flight time of fragment ions relative to the corresponding parent,

$$\begin{aligned} \Delta\tau &= \tau_p - \tau_f = c\sqrt{m_p} - (a\sqrt{m_p} + b\sqrt{m_f}) \\ &= (c - a)\sqrt{m_p} - b\sqrt{m_f} \\ &= b\sqrt{m_p} - b\sqrt{m_f} \\ \Delta\tau &= b(\sqrt{m_p} - \sqrt{m_f}) \end{aligned} \quad 2-6$$

Due to the distances they travel $b = (1/3)c = \sim 1.96$.

2.2 Data Acquisition

As discussed in the Apparatus Overview (Section 2.1) when ions (parent and fragment) hit the detector they produce a voltage at a specific time according to their m/z ratio. This is either 1) collected as a voltage vs. time trace on an oscilloscope and is read using the Digital Scope Labview program or 2) collected on gated integrator and the total signal in a specific time window (mass) is recorded using the Breakout Box Labview program. This program is used for spectroscopy and there are two versions: Breakout Box Dye Laser and Breakout Box IR Laser. The details of both programs have been described previously.^{4,11,12}

2.2.1 Digital Scope

The Digital Scope program is mainly used to measure time of flight (TOF) spectra or difference spectra at a fixed wavelength. This Labview program reads the voltage vs. time waveform information from a digital oscilloscope (Tektronix TDS 524A). A difference spectrum is generated by recording the TOF spectra with the photodissociation laser on and subtracting the spectrum with the laser off. The laser is blocked/unblocked with a mechanical chopper. The program allows user to decide the number of laser shots in each on/off cycle and the number of cycles to average. Typically, we use 5000 shots in each cycle and average 20 cycles. Thus, each file includes 100000 shots averaged, for each on and off. The only difference from the previous studies is that when working with the 10 Hz IR laser, the oscilloscope is triggered at 10 Hz.

2.2.2 Breakout Box Dye Laser

This program is mainly used for electronic spectroscopy. The program communicates with the remote computer which controls the dye laser. This program acts as master while the remote computer acts as slave. The program allows the user to give initial parameters such as scanning range, step size. The dye laser is sent to the starting wavelength, the Breakout Box reads data from up to 3 gated integrator, averaging the results for typically 20 laser shots, then the program sends a pulse to the dye laser to move to the next wavelength step. After getting a response from the dye laser, the cycle is repeated. The gated integrators measure the area under the voltage vs. TOF waveform, over a specific period of time (the gate) and produce a DC value, which is sent to an A/D converted and read by Breakout Box. The user sets these gates to measure the signal for the parent and fragment ion(s).

2.2.3 Breakout Box IR Laser

This program is mainly used for vibrational spectroscopy. The working principle is a little bit different than the dye laser program. The program still communicates with a remote computer which scans the IR wavelengths, but acts as slave to that remote master computer. The user inputs the parameters (starting and ending wavenumber and scan speed), and the parameters are sent to the remote computer. The remote computer starts the scan. The Breakout Box program collects data and asks the master (remote) computer to tell it the correct wavenumber. It then assigns the gated integrator value to that wavelength. We needed to trigger the gated integrators at 10 Hz when working with 10 Hz IR laser.

2.2.4 Data Analysis

Collected data has been analyzed using Igor Pro suite program. The analysis includes the averaging of 4-5 sets of data (number of scan files) for both parent (I_{avp}) and fragment (I_{avf}) ions, and normalizing fragment ions to first parent ions then to laser power. Taking more than one scan eliminates the abnormal oscillations in the individual scans, ensures the reproducibility of the scan, and improves the signal/noise. The normalization is done by assuming the absorption cross section is equal to photodissociation cross section (i.e. dissociation quantum yield=1) and number of excited molecules are linearly dependent on laser power.

By analogy with the Beer-Lambert law, if the laser shines on all the molecules,

$$\frac{I_{avp}}{I_{avp} + I_{avf}} = e^{-\sigma f}$$

where σ is the absorption cross section ($\text{cm}^2/\text{molecule}$) and f is the laser fluence ($\text{photons}/\text{cm}^2$), which are related to I_{avp} and $I_{avp} + I_{avf}$ respectively. Therefore,

$$\sigma = -\ln\left(\frac{I_{avp}}{I_{avp}+I_{avf}}\right) / f \quad 2-7$$

Thus, using this equation, we can normalize the spectra. However, this equation can be further simplified for the cases where the photofragmentation yield is very small ($I_{avf} \ll I_{avp}$).

$$1 - \frac{I_{avp}}{I_{avp} + I_{avf}} = 1 - e^{-\sigma f}$$

$$I_{ratio} = 1 - e^{-\sigma f}$$

where $I_{avp} + I_{avf} \cong I_{avp}$, and $I_{ratio} = \frac{I_{avf}}{I_{avp}}$. The exponential term in the equation is smaller

than 1, so a Taylor expansion can be applied. So,

$$e^{-\sigma f} = 1 - (\sigma f) + (\sigma f)^2 - \dots \cong 1 - \sigma f$$

Therefore,

$$\sigma = I_{ratio}/f \quad 2-8$$

We can compare equations 2-7 and 2-8 to find the range over which equation 2-8 is valid. Table 2-1 shows both methods (explicit, 2-7 and approximation, 2-8) for normalization at various photofragment yields. The approximation is in good agreement with the explicit method until 10% dissociation yield. Therefore, throughout the thesis, unless there is more than 10% dissociation, we use the approximation to normalize the spectra.

Although the laser power is adjusted to be as constant as possible throughout the scan, there are still power changes during the scans. Therefore, a further normalization is done by simply dividing the initially normalized wave to the laser power. This assumes the laser power is proportional to fragmentation. This works well for 1 photon dissociation. For IRMPD, we usually find that the normalized fragment yield is proportional to (laser power)ⁿ, with n=1.2 to 1.5.

Table 2-1 Comparison of normalizations for various dissociation yields

Dissociation Yield (%)	$-\ln \left(\frac{I_{avp}}{I_{avp} + I_{avf}} \right)$	I_{ratio}	% Error
1	0.01005	0.010101	0.50
5	0.051293	0.052632	2.61
10	0.105361	0.111111	5.46
20	0.223144	0.25	12.04
50	0.693147	1	44.27

2.3 Experimental Techniques

Using the setup described in the previous sections, we can use several techniques to study photodissociation spectroscopy. In all of the techniques described below, there are three requirements: 1) the molecule has to absorb the photon(s), 2) the absorbed photon energy is sufficient to break a bond, and 3) the photodissociation yield is non-zero.

2.3.1 Mass Spectra and Difference Spectra

To optimize signal for the parent ion of interest, we use a constant voltage (V in section 2.1) on the mass gate so that all the ions make it to the detector. Because ions with different m/z ratios have different flight times, this produces a TOF spectrum, which can be converted to a parent ion mass spectrum using equation 2-3.

After getting the mass spectra, we can now pulse the mass gate to allow only the desired ions to make it to the detector. As described earlier, the mass gate delay time and width is calculated from a known ion with equation 2-4. When the photodissociation laser is off (or

blocked), only parent ions are collected at the corresponding time calculated by 2-3. When the dissociation laser is on (or unblocked), parent ions still arrive at the same time, but in decreased amounts and fragment ions (with the time given by equation 2-5) are appeared. By subtracting the spectrum of laser-off from laser-on, the difference spectrum is measured.

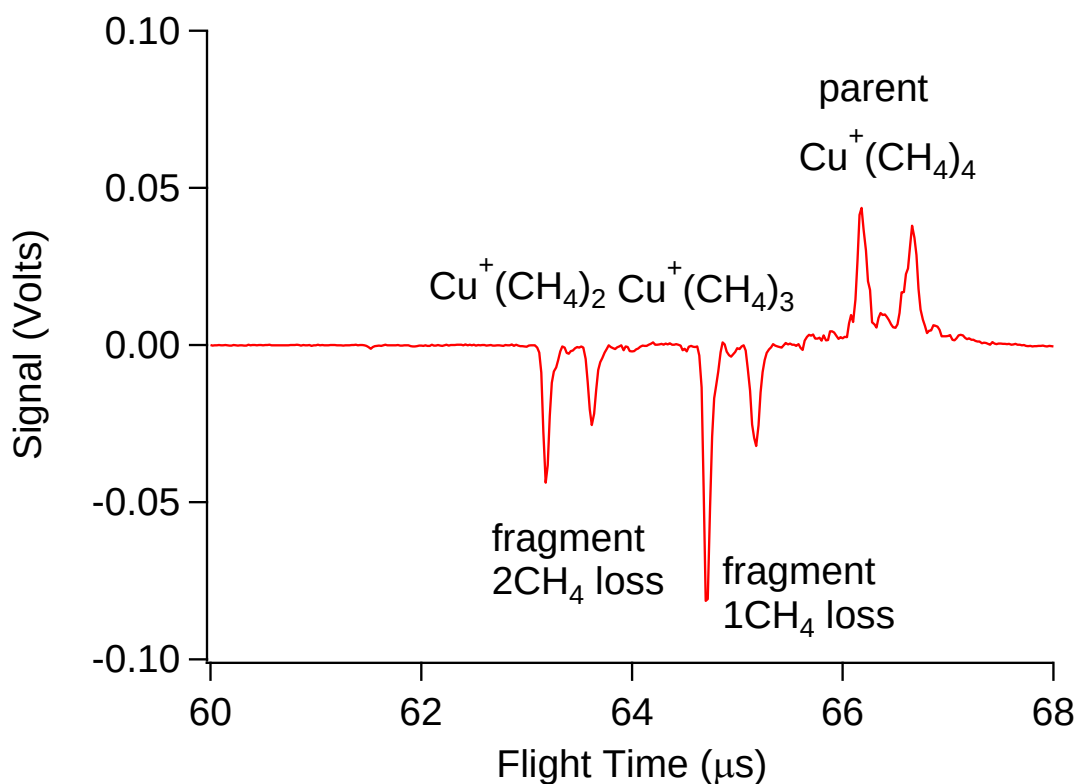


Figure 2.4 Difference Spectrum of $\text{Cu}^+(\text{CH}_4)_4$ with IR laser at 2767 cm^{-1} . The doublets are due to the naturally occurring Cu-63 and Cu-65 isotope

From the difference spectra, we can get information about the dissociation products. Figure 2.4 shows the difference spectrum of $\text{Cu}^+(\text{CH}_4)_4$ at 2767 cm^{-1} . The spectrum shows that dissociation occurs by loss of one or two CH_4 ligands. No H_2 loss is observed suggesting that methane is not activated. This will be further explained in chapters 4 and 5.

2.3.2 Electronic Photodissociation Spectroscopy

After finding the dissociation products at a fixed wavelength, we use the Breakout Box Dye Laser program (Section 2.2.2) to scan the photodissociation laser (the dye laser in this case) in order to measure the photodissociation spectrum.

As mentioned in Chapter 1, we typically study molecules that undergo indirect photodissociation. This typically leads to a vibrationally, and maybe even rotationally, resolved spectrum. When this is the case, the electronic spectrum gives information about the vibrational modes, quantum numbering, dissociation energies and bond energies. In addition, the spectrum may be rotationally partially resolved and gives useful information about the molecular geometry. Thus, electronic photodissociation spectroscopy provides information about the excited electronic states, symmetry of the excited state and upper limits for binding energies. Sometimes, it may even provide binding energies with high precision.

Our group has successfully applied electronic spectroscopy to $\text{Co}^+(\text{H}_2\text{O})$ and its isotopomers (discussed in detail in Chapter-3). The studies have been extended to $\text{Ni}^+(\text{H}_2\text{O})$ and $\text{Mn}^+(\text{H}_2\text{O})$.

2.3.3 Vibrational Spectroscopy

IR spectroscopy gives information about the ground electronic states such as bonding and geometry. The IR photodissociation laser is scanned in the C-H or O-H stretching region, when the laser wavelength is resonant with either of the stretches, the molecule will absorb the

light. If the absorbed energy is enough to break any bond in the molecule, photodissociation occurs and fragment ions are measured. Since the single IR photon energy is relatively small ($\sim 3000\text{ cm}^{-1} = 36\text{ kJ/mol}$), photodissociation occurs only for limited molecules. In order to overcome this limitation, vibrational spectroscopy can be mainly applied in three different ways.

2.3.3.1 IR Single Photon Dissociation (IRPD)

This technique is the simplest way of measuring the vibrational spectra. In this method, since the molecule's binding energy is weaker than the IR photon energy, the molecule absorbs the light when the photon energy is in resonance with one of the vibrational frequencies and predissociates (Figure 2.5). Photodissociation does not necessarily occur at the bond that is absorbing the light. Instead, intramolecular vibrational redistribution (IVR) occurs on a sub-microsecond (and often sub-nanosecond) timescale, depending on the size of the molecule. The photon energy is re-distributed throughout the molecule, and the weakest bond breaks (predissociation). In our experiments, the $M^+(\text{CH}_4)_n$ (where $M=\text{Co, Ni, Cu, Ag}$ and $n\geq 3$) complexes show predissociation. The photodissociation yield is generally high for predissociation ($>5\%$).

2.3.3.2 IR Multiple Photon Dissociation (IRMPD)

The molecules that have binding energies bigger than the IR photon energy ($>4000\text{ cm}^{-1}$) are not simply photodissociated by IR single photon. However, several groups have developed complementary techniques to measure vibrational spectra of strongly bound molecules.¹³ One way to study them is to use IR Multiple Photon Dissociation, in which several photons are absorbed by the molecule and thus the molecule can dissociate. (Figure 2.5) Photodissociation requires the molecule to absorb enough photons so that their total energy is enough to break the weakest bond. IRMPD also requires the energy absorbed in one vibrational mode to be easily distributed to other modes. A high density of vibrational states and anharmonicity enable

the efficient IVR process. During our experiments, the vibrational spectra of $\text{Ag}^+(\text{CH}_4)_{1-2}$ complexes are measured with IRMPD. Similarly, we attempted to measure spectra of $\text{Co}^+(\text{CH}_4)_{1-2}$ and $\text{Ni}^+(\text{CH}_4)_{1-2}$ with IRMPD.

Small molecules are expected to have less density of vibrational states and hence low IVR rates. For these reasons, for small molecules with big binding energies, the IRMPD yield is very small, in most cases it is zero (<1%). In addition to low dissociation yield, power broadening and preferential dissociation of hotter ions lead to a broad and unresolved spectrum, which does not usually provide useful structural information.¹⁴

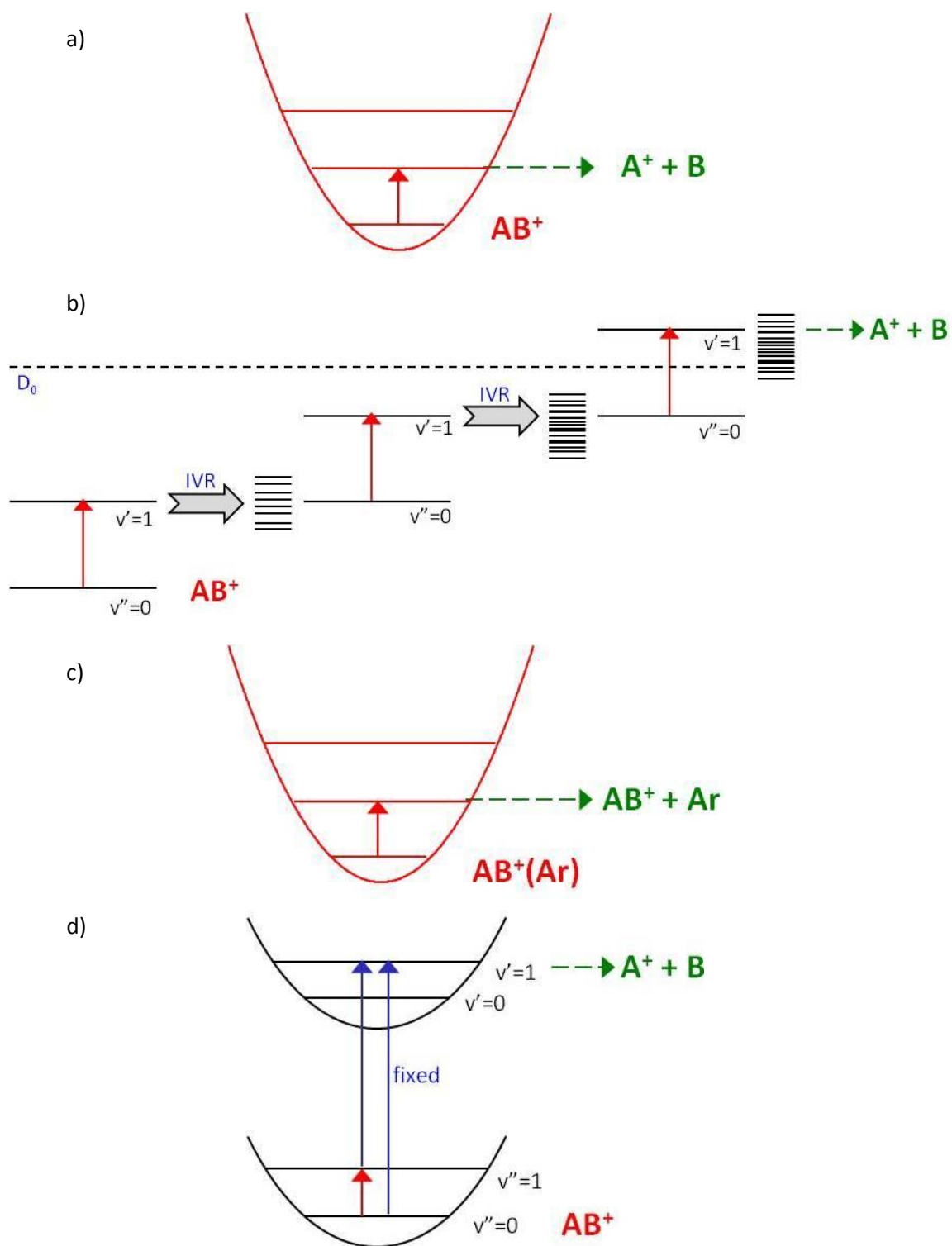


Figure 2.5 Schematic illustration of techniques used for vibrational spectroscopy a) Infrared Predissociation b) Infrared Multiple Photon Dissociation (IRMPD) c) Ar-tagging d) Vibrationally Mediated Photodissociation (Depletion)

2.3.3.3 Argon Tagging

Another approach to measure IR spectra of small molecules with large binding energies is to tag them with an inert, weakly bound atom or molecule that does not perturb the target molecule's vibrations. Absorption of one photon leads to dissociation by loss of the tag. The tagged molecule in most cases is argon and so the technique is called Argon-tagging.¹⁴⁻¹⁸ Two key points with this technique is to have an Ar binding energy that is smaller than the IR photon energy (so that it dissociates) and to have Ar not perturb the spectrum. Since in most cases, Ar binds very weakly, producing Ar-tagged ions requires that the ions be cold. Recall that the ions are produced and cooled to rotational temperatures of 8-15 K in the laser ablation source and subsequent expansion into vacuum. However, the vibrational temperature can be significantly higher. So, Ar-tagging also ensures that the ions' vibrations are very cold. Thus, the Ar-tagging spectrum gives much sharper and more intense peaks than IRMPD. In our experiments, we used Ar-tagging to measure vibrational spectra of $M^+(\text{CH}_4)_{1-2}$, where $M=\text{Co, Ni and Cu}$.

2.3.4 Vibrationally Mediated Photodissociation (VMP)

So far, we have discussed electronic spectroscopy, which provides information about vibrational and rotational structure in the excited electronic states, and vibrational spectroscopy, which provides information about the vibrations in the ground electronic state. Electronic spectroscopy and vibrational spectroscopy can be combined to study a molecule's ground and excited states in more detail. This is typically applied to small, strongly bound molecules, in order to measure spectra of untagged molecules, with laser-limited resolution. This combination, called Vibrationally Mediated Photodissociation (VMP) spectroscopy, can be done in different ways according to the purpose. If the aim is to study the vibrational spectroscopy of ground electronic state, depletion experiments can be run. In this double

resonance experiments, the idea is to fix the dye laser to a known electronic transition and scan the IR. When the IR laser comes into resonance with a vibration in the ground electronic state, the number of molecules in the ground vibrational state of the ground electronic state will decrease due to the transition, so fewer molecules will be excited by the dye laser and there will be less dissociation. This will create depletions where the IR is absorbed (at the vibrational frequencies in the ground electronic state) (Figure 2.5) Once the vibrational frequency has been measured, the IR can be fixed to a resonance and the dye laser can be scanned. For studying the vibrations in the ground electronic state, VMP has the great advantage over IRMPD and Ar-tagging that it does give unperturbed and un-broadened peaks. In our studies, we have measured the O-H stretches of $\text{Co}^+(\text{H}_2\text{O})$ using VMP (Chapter 3).

These double resonance experiments require critical timing. The IR laser should shine before the dye laser. This is because the IR first needs to vibrationally excite some molecules, then the VIS laser should dissociate the remainder of the molecules. The delay time between the IR and VIS lasers can be optimized by monitoring the amount of depletion while varying the delay, as shown in Figure 2.6. We found the best delay to be 20-40 ns.

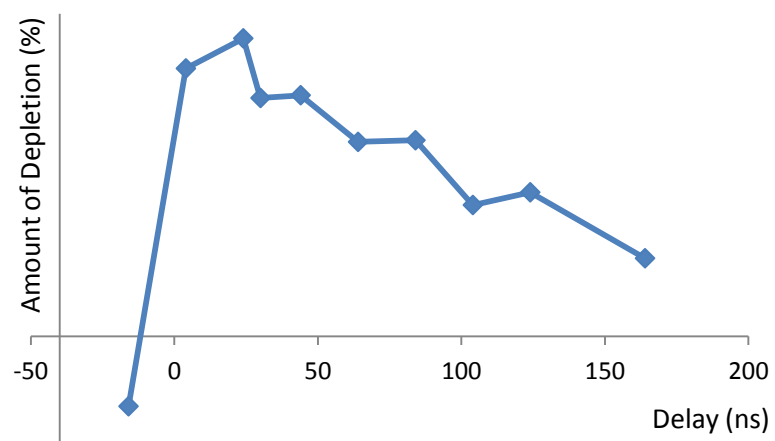


Figure 2.6 Dependence of relative depletion on the IR-VIS laser delay Depletion in dissociation of $\text{Co}^+(\text{H}_2\text{O})$ at 13968 cm^{-1} (VIS) when the IR laser is at the O-H antisymmetric stretch, 3692 cm^{-1} .

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CHAPTER 3
ELECTRONIC AND VIBRATIONALLY MEDIATED PHOTODISSOCIATION SPECTROSCOPY OF
Co⁺(H₂O) AND ISOTOPOMERS

3.1 Introduction

As noted in Chapter 1, the important role that metal-water interactions play in solvation, catalysis and biology has motivated many experimental and computational investigations of metal ion-water complexes. In particular, gas-phase studies permit direct, detailed examination of the intrinsic interactions between metal ions and specific numbers of water molecules.¹ The binding energies of water molecules to first-row transition metal cations M⁺ were first measured by Magnera, David and Michl² and Marinelli and Squires³ using collision-induced dissociation (CID) in a triple-quadrupole mass spectrometer and were later refined in a guided-ion beam (GIB) measurement by Dalleska, Honma, Sunderlin and Armentrout.⁴

The Co⁺(H₂O) complex is of particular interest because Co⁺ binds especially strongly to ligands, as illustrated by the experimental Co⁺-H₂O bond dissociation energies: 155±12 kJ/mol,² 168±16 kJ/mol,³ and 161±7 kJ/mol.⁴ This strong non-covalent interaction is due to the cobalt ion's 3d⁸ (³F₄) ground state.⁵ Metal cations with 3dⁿ electronic configurations bind more strongly than those with 3dⁿ⁻¹ 4s¹ configurations, since the 3d orbitals are smaller and more directional than the 4s, reducing metal-ligand repulsion, consequently allowing the metal to get closer to the ligand. One potential implication of this strong bond is the recent proposal that cobalt ion-water interactions are the key to efficient Co²⁺/Co⁺ reduction in the cobalamine (vitamin B₁₂) cofactor of methyltransferases.⁶

There have been numerous spectroscopic studies of M⁺(H₂O). This includes electronic spectroscopy of hydrated alkaline earth cations Mg⁺(H₂O)⁷⁻¹⁰, Ca⁺(H₂O)^{11,12} and Sr⁺(H₂O)¹³⁻¹⁵ and transition metal cations V⁺(H₂O),¹⁶ Ni⁺(H₂O)¹⁷ and Zn⁺(H₂O)¹⁸. Poisson *et al.* studied photolysis of

$\text{Co}^+(\text{H}_2\text{O})_n$ ($n=1-10$) at 532, 355 and 266 nm, but observed no photodissociation of $\text{Co}^+(\text{H}_2\text{O})$.¹⁹ In studies of hydrated Co(II) cluster ions, our group measured the electronic spectra of $\text{Co}^{2+}(\text{H}_2\text{O})_n$ ($n=4-7$) in the visible via photodissociation,²⁰ and Donald *et al.* photoexcited $\text{M}^{2+}(\text{H}_2\text{O})_n$ ($\text{M}=\text{Mn}, \text{Fe}, \text{Co}, \text{Cu}$; $n=19-124$) at 193 and 248 nm to determine H_2O ligand binding energies.²¹

In addition, Brucat and coworkers measured electronic spectra of $\text{Co}^+(\text{L})$ complexes for $\text{L}=\text{Ar}, \text{Kr}, \text{Xe}$,²²⁻²⁴ CO_2 ,^{25,26} and N_2 .²⁷ Duncan and coworkers recently obtained the electronic spectrum of $\text{Co}^+(\text{Ne})$.²⁸ The photodissociation spectra of these complexes extend throughout the visible, with vibrationally- and, often, rotationally-resolved transitions to several excited states. The spectra are similar, as they represent metal-centered transitions between states arising from the d^8 ($^3\text{F}_4$) Co^+ ground state and states correlated to d^7s (^3F) and d^8 (^3P) excited states of Co^+ . Analysis of the spectra reveals metal-ligand bond lengths, excited state vibrational frequencies, and diabatic dissociation energies for the ground and excited electronic states.

Vibrational spectra of several transition metal $\text{M}^+(\text{H}_2\text{O})_n$ have also been measured, in the O-H stretching region. These spectra elucidate the cation's effect on the ligands' bonds and, for larger clusters, reveal hydrogen-bonding networks. Duncan and coworkers have used argon tagging to measure vibrational spectra of $\text{M}^+(\text{H}_2\text{O})$ ($\text{M}=\text{Sc}$,²⁹ V ,^{30,31} Cr ,³² Mn ,³³ Fe ,^{34,35} Ni ,³⁶ Cu ³⁷) and $\text{M}^{2+}(\text{H}_2\text{O})$ ($\text{M}=\text{Sc}$,²⁹ V ,³⁸ Cr ,³² Mn ,³³) in the O-H stretching region. The vibrational spectrum of $\text{Co}^+(\text{H}_2\text{O})$ has not been previously published, although Furukawa *et al.* measured the photodissociation spectra of $\text{Co}^+(\text{H}_2\text{O})_n$ ($n=4-6$) in the O-H stretching region.³⁹ In addition, O'Brien and Williams used vibrational spectra of solvated, multiply charged ions $\text{M}^{2+}(\text{H}_2\text{O})_n$ ($\text{M}=\text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$; $n=5-8$) in the O-H stretching region to determine the coordination number of the metal ion.⁴⁰

Several groups have also calculated the structure and binding energies of $\text{Co}^+(\text{H}_2\text{O})$.⁴¹⁻⁴⁵ The $\text{Co}^+(\text{H}_2\text{O})$ complex is calculated to be planar, with C_{2v} symmetry. This picture is complicated

by the computational prediction of four low-lying electronic states whose energies are so similar that the calculated ground state depends on the level of theory.

Electronic spectroscopy of $M^+(H_2O)$ potentially allows one the ability to measure bond dissociation energies, vibrational frequencies of excited electronic states, excited state dissociation energies and rotational structure. This, in turn, can be used to determine the geometries of the ground and excited electronic states. Vibrational spectra of $M^+(H_2O)$ reveal how metal ions affects bonds in the H_2O ligand. Our group used photodissociation spectroscopy and vibrationally mediated photodissociation (VMP) to measure the electronic spectrum and O-H stretching frequencies of $Ni^+(H_2O)$.¹⁷ The current experiments extend this work to the $Co^+(H_2O)$ complex and its isotopomers.

3.2 Experimental Methods

The Co^+ , formed by laser ablation of a cobalt rod, interacts with a gas mix of 0.1-0.4% H_2O seeded in helium at 30 psi backing pressure introduced through a pulsed piezoelectric valve to form $Co^+(H_2O)$. For electronic spectroscopy studies, a wavelength range of 543-740 nm was scanned with a Continuum ND6000 dye laser at a line width of 0.1 cm^{-1} using a variety of laser dyes. The dye laser wavelength is calibrated using the optogalvanic spectrum of neon; the IR laser is calibrated using the absorption spectrum of water vapor. The spectra of $Co^+(HOD)$, $Co^+(D_2O)$ and $Co^+(H_2^{18}O)$ were also measured to aid in analyzing and assigning the spectrum. They were produced using a H_2O/D_2O mixture, pure D_2O , and $H_2^{18}O$ (Cambridge Isotope Labs) in the carrier gas respectively.

The computational studies used the *Gaussian 09* suite of programs.⁴⁶ The geometries, relative energies and vibrational frequencies of low-lying states of $Co^+(H_2O)$ were calculated with the B3LYP and BHandHLYP hybrid density functionals with the 6-311++G(3df,p) basis set.

Higher-lying excited states were calculated using time-dependent density functional theory (TD-DFT). In addition, the geometries and relative energies of low-lying states of $\text{Co}^+(\text{H}_2\text{O})$ were calculated at the CCSD(T)/aug-cc-pVTZ level, as was the Co-O stretch potential.

3.3 Results and Discussion

3.3.1 Electronic Spectroscopy

Photodissociation studies of $\text{Co}^+(\text{H}_2\text{O})$ and its isotopomers $\text{Co}^+(\text{HOD})$, $\text{Co}^+(\text{D}_2\text{O})$ and $\text{Co}^+(\text{H}_2^{18}\text{O})$ were carried out from 13500 cm^{-1} to 18400 cm^{-1} . In this wavelength region, only one active dissociation channel, cobalt cation + water, is observed. This is not surprising, as production of $\text{CoOH}^+ + \text{H}$ from $\text{Co}^+(\text{H}_2\text{O})$ is endothermic by 360 kJ/mol ,⁴⁷ requiring wavelengths below 332 nm to dissociate. The electronic spectrum was thus obtained by monitoring the Co^+ fragment from photolysis of $\text{Co}^+(\text{H}_2\text{O})$ and its isotopomers. The photodissociation spectrum is structured with well-resolved vibrational features and partially resolved rotational structure as illustrated in Figure 3.1.

The electronic spectrum is similar to those of other $\text{Co}^+(\text{L})$ ($\text{L}=\text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}, \text{CO}_2$) complexes, which show transitions to several excited electronic states, with long progressions in the metal-ligand stretch.^{22-26,28} Here, a number of the vibrational features are single, sharp peaks, while others are multiplets (typically triplets). This is similar to rotational structure observed in the electronic spectra of $\text{Mg}^+(\text{H}_2\text{O})$,⁸⁻¹⁰ $\text{Ca}^+(\text{H}_2\text{O})$,^{11,12} $\text{Ni}^+(\text{H}_2\text{O})$ ¹⁷ and $\text{Zn}^+(\text{H}_2\text{O})$.¹⁸ These molecules are near-prolate tops. Rotation about the M-O bond (the a axis) has a small moment of inertia (only the hydrogen atoms are off axis), and hence a large A rotational constant of $\sim 14\text{ cm}^{-1}$. The B and C rotational constants are much smaller and nearly equal ($\sim 0.25\text{ cm}^{-1}$, depending on the metal and the M-O bond length). The sharp single peaks such as the one at 13964 cm^{-1} (B1 in Figure 3.1) are due to parallel bands, $\Delta K_a=0$.

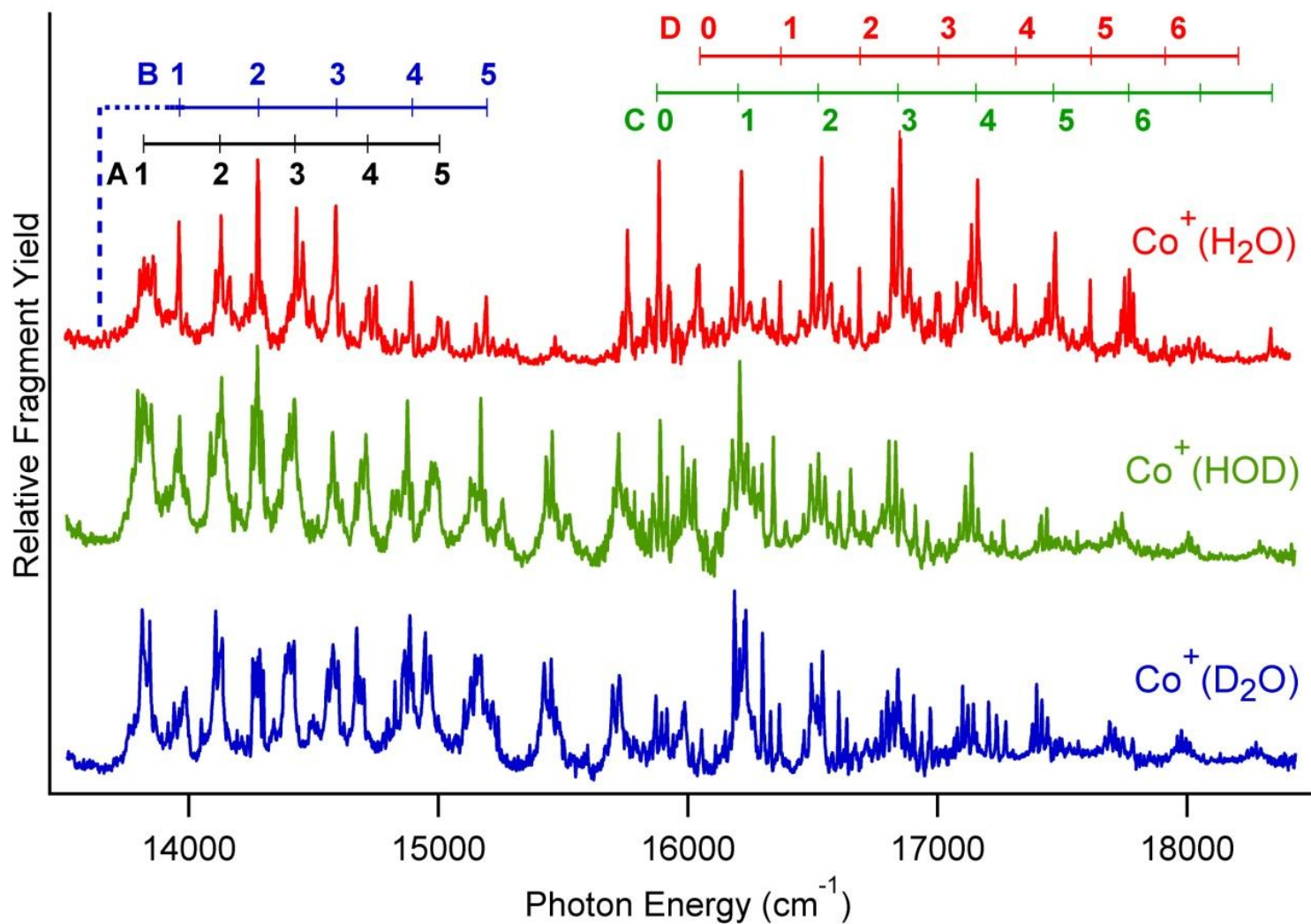


Figure 3.1 Photodissociation spectra of the $\text{Co}^+(\text{H}_2\text{O})$, $\text{Co}^+(\text{HOD})$ and $\text{Co}^+(\text{D}_2\text{O})$ complexes from 13500 to 18400 cm^{-1} . The combs indicate the Co-water stretch quantum number ν_3' in each of the four electronic states observed.

Perpendicular bands, which have $\Delta K_a = \pm 1$, lead to several peaks spaced by $\sim 30 \text{ cm}^{-1}$, (as is observed near 13808 cm^{-1} for $\text{Co}^+(\text{H}_2\text{O})$) as several initial K_a states are populated even at the $\sim 15\text{K}$ rotational temperature. Thus the spectrum consists of four different vibrational progressions, two of which are parallel bands (labeled **B** and **D**) while the other two are perpendicular bands (labeled **A** and **C**). In order to determine whether these are due to four different electronic states or to combinations of vibrations, and to assign the vibrational progressions, spectra of isotopomers were measured, and the geometries, rotational constants and vibrational frequencies of the ground and several excited states of $\text{Co}^+(\text{H}_2\text{O})$ were calculated.

The nature of the ground state of $\text{Co}^+(\text{H}_2\text{O})$ has been the subject of several studies. Early calculations by Rosi and Bauschlicher using the modified coupled-pair functional method showed that interaction of ground state $\text{Co}^+ (d^8, {}^3F)$ with H_2O leads to four low-lying states.⁴¹ Rosi and Bauschlicher predict the ground state to be ${}^3B_1$, with the nearly degenerate ${}^3A_2$ and ${}^3A_1$ states 245 cm^{-1} higher in energy and the ${}^3B_2$ state at 630 cm^{-1} .⁴⁸ The results of several calculations,⁴¹⁻⁴⁵ all of which predict a ${}^3B_1$ or ${}^3A_2$ ground state, are summarized in Table 3-1.

The geometries of the four low-lying states of $\text{Co}^+(\text{H}_2\text{O})$ were optimized at the B3LYP/6-311++G(3df,p), BHandHLYP/6-311++G(3df,p), and CCSD(T)/aug-cc-pVTZ levels. In each case, the ${}^3B_1$, ${}^3A_2$ and ${}^3A_1$ states are nearly degenerate. The ${}^3B_2$ state lies somewhat higher in energy and distorts from C_{2v} to C_s symmetry by out-of-plane hydrogen bending. The ground state was calculated to be the ${}^3A_2$ state with B3LYP and BHandHLYP and ${}^3B_1$ with CCSD(T). As will be discussed later, the experiments determine the ground state to be ${}^3B_1$. Molecular orbitals for the ${}^3B_1$ state are shown in Figure 3.2. In C_{2v} symmetry, the 3d orbitals on Co^+ lead to $3d\sigma(z^2)$ and $3d\delta(x^2-y^2)$ with a_1 symmetry, $3d\delta(xy)$ with a_2 symmetry, $3d\pi(xz)$ with b_1 symmetry, and $3d\pi(yz)$ with b_2 symmetry. In the ${}^3B_1$ state, the $3d\sigma(z^2)$ and $3d\delta(x^2-y^2)$ orbitals mix. One hole is in this mixed a_1 orbital, and the second hole is in the b_1 orbital. This mixing was also observed by Rosi and Bauschlicher.⁴¹

Table 3-1 Calculated energies and geometries of low-lying states of $\text{Co}^+(\text{H}_2\text{O})$

Method/Basis	State	$r_{\text{Co-O}}$ (Å)	$r_{\text{O-H}}$ (Å)	$\angle \text{HOH}$	Energy (cm^{-1})	Orbital Occupancy (Holes)
MCPF (Ref. 30a)	$^3A_1$				~245	$3d\delta(x^2-y^2)$, $3d\sigma(z^2)$
	$^3A_2$	2.022			245	$3d\delta(xy)$, $3d\sigma(z^2)$
	$^3B_1$	1.991			0	$[3d\delta(x^2-y^2), 3d\pi(xz)] + [3d\sigma(z^2), 3d\pi(xz)]$
	$^3B_2$				630	$3d\delta(xy)$, $3d\pi(xz)$
CCSD(T)(FULL)/6- 311++G**//MP2(FULL)/6- 311++G** (Ref. 30b)	$^3A_1$				14	$3d\delta(x^2-y^2)$, $3d\sigma(z^2)$
	$^3A_2$	2.003	0.964	106.6	0	$3d\delta(xy)$, $3d\sigma(z^2)$
	$^3B_1$	1.973	0.965	106.6	115	$3d\delta(x^2-y^2)$, $3d\pi(xz)$
	$^3A''$					$3d\delta(x^2-y^2)$, $3d\pi(yz)$
B3LYP/B3// B3LYP/B2 (Ref. 30d)	$^3A_1$	1.988			175	
	$^3A_2$	1.985			175	
	$^3B_1$	1.960			0	
	$^3B_2$	1.992			944	
MR-SDCI(+Q) (Ref. 30e)	$^3A_1$				35	
	$^3A_2$	1.944	0.967	108.1	0	$3dz^2$, $3dxy$
	$^3B_1$				245	
	$^3B_2$				105	
CCSD(T)/aug-cc-pVTZ (This work)	$^3A_1$	2.0003	0.964	106.7	39	$3d\sigma(z^2)$, $3d\delta(x^2-y^2)$
	$^3A_2$	1.9996	0.964	106.8	25	$3d\sigma(z^2)$, $3d\delta(xy)$
	$^3B_1$	1.9705	0.965	106.8	0	$[3d\delta(x^2-y^2), 3d\pi(xz)] + [3d\sigma(z^2), 3d\pi(xz)]$

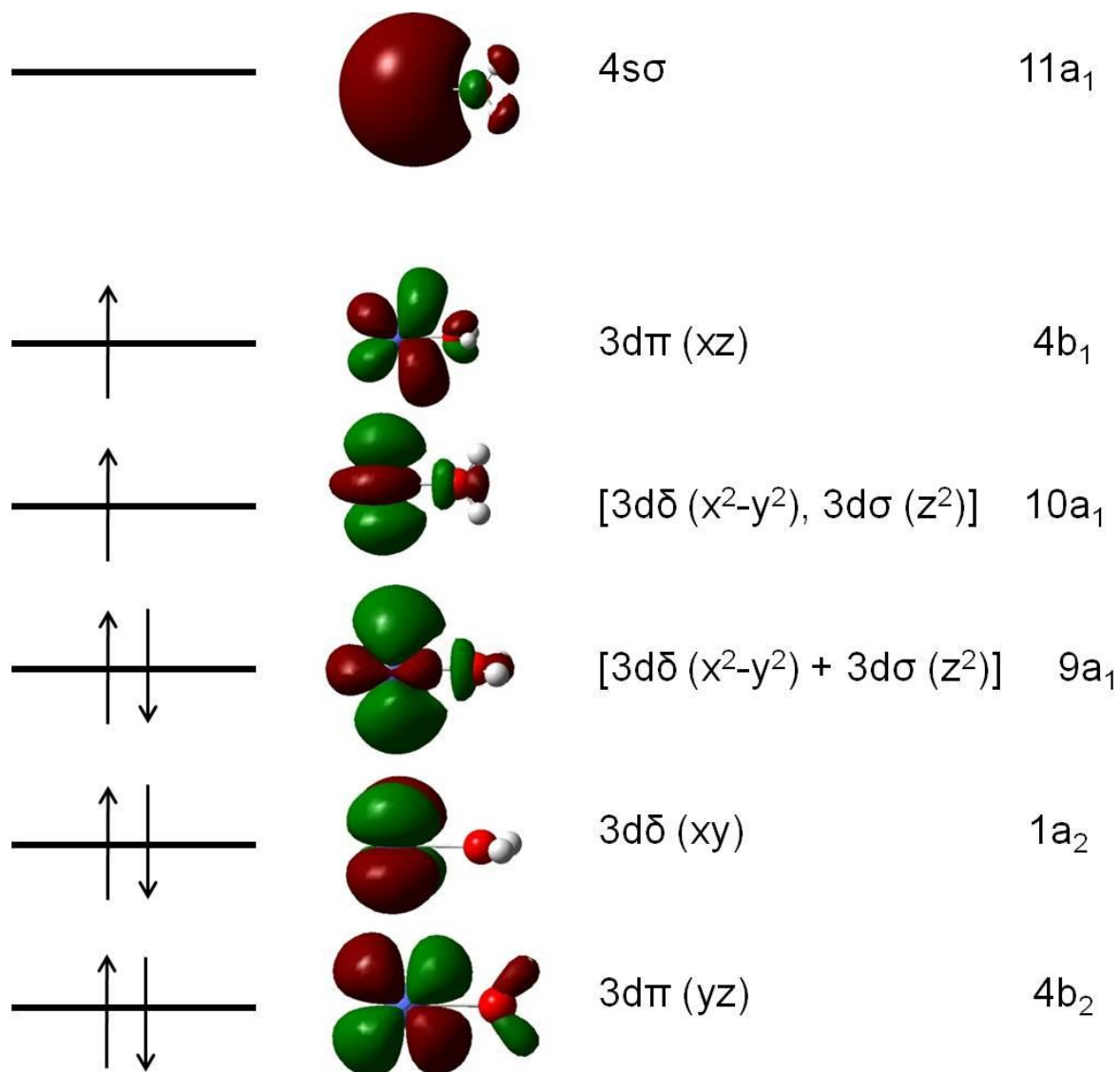


Figure 3.2 Molecular orbital diagram and orbital occupancy of $\text{Co}^+(\text{H}_2\text{O}) \text{X}, {}^3\text{B}_1$

The orbital occupancies and low-lying electronic states of $\text{Co}^+(\text{H}_2\text{O})$ are related to those of the $\text{Co}^+(\text{rare gas})$ complexes. The ground state of $\text{Co}^+(\text{Ar})$ is ${}^3\Delta_3$, with holes in the 3dδ and 3dσ orbitals.^{23,49} In $\text{Co}^+(\text{H}_2\text{O})$ this corresponds to the ${}^3\text{A}_1$ and ${}^3\text{A}_2$ low-lying excited states. These two states are nearly degenerate in C_{2v} symmetry and would be degenerate in $\text{C}_{\infty v}$. The first excited state of $\text{Co}^+(\text{Ar})$ is ${}^3\Pi$. At the MRCI+Q level, this state is 476 cm^{-1} above the ground state.⁴⁹ It has holes in the 3dπ and 3dσ orbitals, with some contribution from a configuration with holes in the 3dπ and 3dδ orbitals. This state corresponds to the ${}^3\text{B}_1$ ground state of $\text{Co}^+(\text{H}_2\text{O})$. The other two

low-lying excited states of $\text{Co}^+(\text{Ar})$ are the $^3\Sigma$ (782 cm^{-1}) with contributions from states with two $3d\pi$ holes and two $3d\delta$ holes and the $^3\Phi$ (855 cm^{-1}) with holes in the $3d\pi$ and $3d\delta$ orbitals

The $\text{Co}^+(\text{H}_2\text{O})$ molecule has six vibrations, whose calculated frequencies are shown in Table 3-2. The three high-frequency vibrations are essentially perturbed H_2O vibrations. There are also three low-frequency vibrations: the Co-O stretch and two H_2O hindered rotations (bends). Five of the six vibrations primarily correspond to hydrogen atom motion. Thus, substitution of deuterium for hydrogen should lead to large isotopic shifts in these frequencies, while the Co-O stretch should show only a small H/D isotopic shift. Experimentally, each band (**A-D**) consists of a series of peaks separated by $\sim 320\text{ cm}^{-1}$. This spacing decreases slightly at higher energy due to vibrational anharmonicity. Upon complete deuteration, the peak spacing decreases, but only by $10\text{-}15\text{ cm}^{-1}$. Therefore, the observed vibrations are assigned to a progression in the Co-O stretch (ν_3') and each band (**A-D**) corresponds to a transition to a different electronic state.

The first peak observed in the photodissociation spectrum is not necessarily the transition to $\nu'=0$, as this transition might lie below the dissociation energy. Therefore, the origin band, and so the vibrational quantum numbering, is not clear from the $\text{Co}^+(\text{H}_2\text{O})$ spectrum, but can be determined using isotopic shifts. For an electronic transition between two Morse oscillators, the shift is given by

$$\Delta E_{iso} = \omega_{e3}'(1 - \rho_3)\nu_3' - \omega_{ex_{e3}}'(1 - \rho_3^2)(\nu_3')(\nu_3' + 1) + \Delta T_{00} \quad 3-1$$

where ω_{e3}' and $\omega_{ex_{e3}}'$ are the upper state frequency and anharmonicity, ΔE_{iso} is the difference in the $\nu_3' \leftarrow \nu_3''=0$ transition energy between the light (L) and heavy (H) isotopomers, $\rho_3 =$

$$\sqrt{\frac{\mu_3^L}{\mu_3^H}} \text{ and } \Delta T_{00} \text{ is the difference in the origin transition between the two isotopomers.}$$

Table 3-2 Experimental and calculated vibrational frequencies of $\text{Co}^+(\text{H}_2\text{O})$ and $\text{Co}^+(\text{D}_2\text{O})$. The frequencies at the BHandHLYP/6-311++G(3df,p) level are scaled by 0.92. By binding to Co^+ , the symmetric and antisymmetric stretches of H_2O red shift by 47 and 76 cm^{-1} , respectively.

Vibrational Symmetry	Mode (ν_i)	Description	Frequency (cm^{-1}) $\text{Co}^+(\text{H}_2\text{O})$ BHandHLYP	Frequency (cm^{-1}) $\text{Co}^+(\text{D}_2\text{O})$ BHandHLYP	Frequency (cm^{-1}) $\text{Co}^+(\text{H}_2\text{O})$ Experimental	Frequency (cm^{-1}) H_2O	Frequency (cm^{-1}) D_2O
a_1	1	H-O-H symmetric stretch	3604	2626	3609.7 ± 1	3657	2671
	2	H-O-H bend	1575	1169		1595	1178
	3	Co-O stretch	354	343		-	-
b_1	4	Out-of-plane bend	318	246		-	-
b_2	5	H-O-H antisymmetric stretch	3674	2725	3679.5 ± 2	3756	2788
	6	In-plane bend	538	405		-	-

In principle, in order to determine the quantum numbering of the transitions, the observed energy shift can be used between any two of $\text{Co}^+(\text{H}_2\text{O})$, $\text{Co}^+(\text{HOD})$, and $\text{Co}^+(\text{D}_2\text{O})$. However, hydrogen-to-deuterium substitution leads to two complications. The first is that it significantly changes the A rotational constant and thus the appearance of the perpendicular bands. Rotational simulations of each vibrational feature would thus be required to determine the isotopic shift. The second difficulty is that H/D substitution leads to large frequency shifts in five of the six vibrations. If the frequencies of these vibrations are different in the ground and excited electronic states, ΔT_{00} in 3-1 is non-negligible. It is difficult to quantify this effect, as only two of these vibrational frequencies (ν_1'' and ν_5'') are measured. Clearly, isotopic substitution at Co or O is preferable. Cobalt-59 is the only stable isotope. So, isotopic shifts were measured using H_2^{18}O . This has two advantages: H_2^{18}O does not affect the A rotational constant, as the oxygen lies on the a axis, and the shift in the zero point energy is small. Lessen *et al.* also used ^{18}O substitution to assign the vibrational quantum numbering in $\text{V}^+(\text{H}_2\text{O})$.¹⁶

Figure 3.3 shows the observed shift from $\text{Co}^+(\text{H}_2^{16}\text{O})$ to $\text{Co}^+(\text{H}_2^{18}\text{O})$ for the first three peaks in each of the four electronic states. For the higher-energy bands, **C** and **D**, the observed shifts lie along the solid line, indicating that the first observed peak is due to the $\nu_3'=0 \leftarrow \nu_3''=0$ transition. However, for the low-energy bands, **A** and **B**, the shifts lie along the upper, dashed line, so the first peak observed is due to the $\nu_3'=1 \leftarrow \nu_3''=0$ transition. Once the quantum numbers have been assigned, the Co-O stretching frequencies and anharmonicities in each excited electronic state can be calculated. The results are summarized in Table 3-3. All of the excited states have similar Co-O stretching frequencies of $\nu_3' \approx 325 \text{ cm}^{-1}$. This is substantially lower than the calculated CCSD(T)/aug-cc-pVTZ value for the ground state: $\nu_3''=400 \text{ cm}^{-1}$.

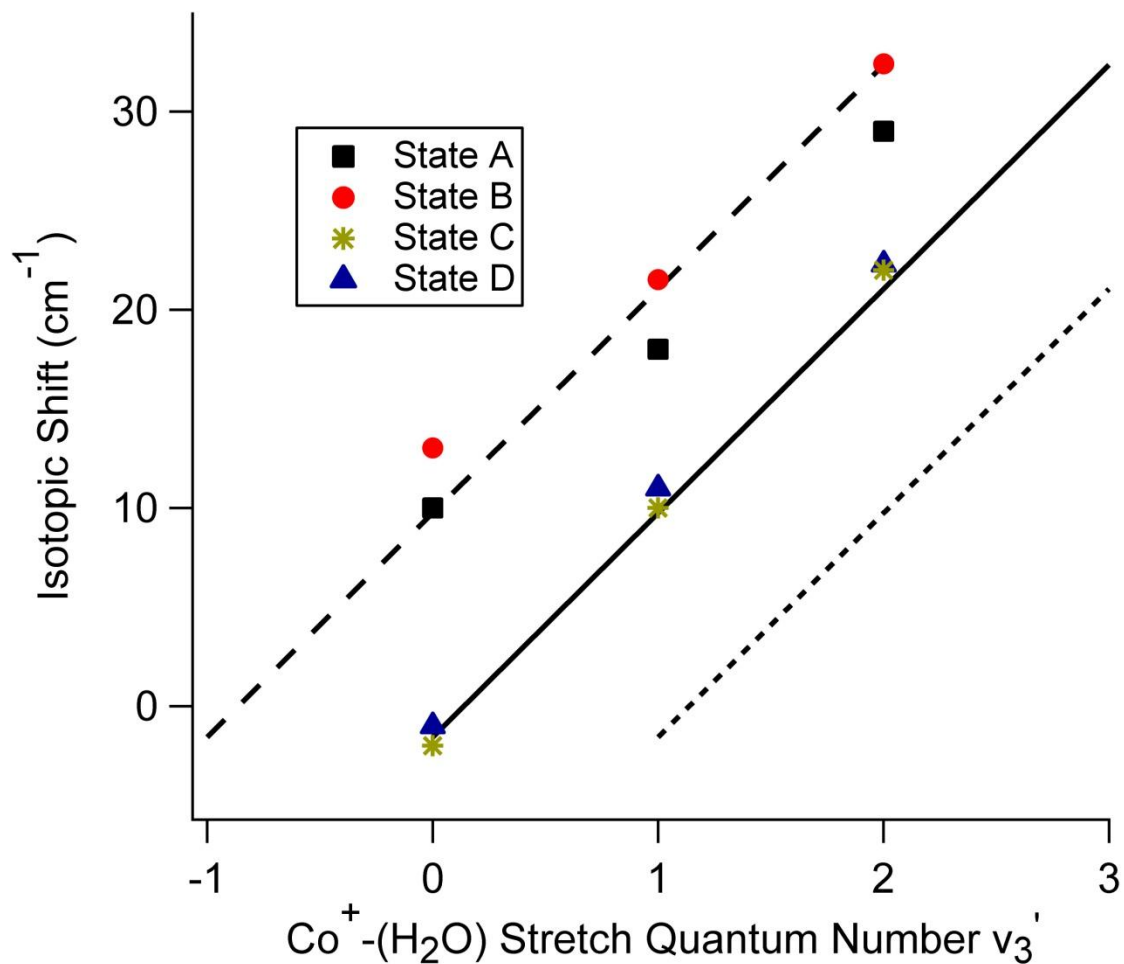


Figure 3.3 Assignment of the cobalt-water stretch vibrational quantum numbering for the four electronic states observed in the photodissociation spectrum of Co⁺(H₂O). Experimental shifts of Co⁺(H₂¹⁶O) vs. Co⁺(H₂¹⁸O) are compared to values calculated assuming the first peak observed is due to v₃'=1 ← v₃''=0 (dashed line), v₃'=0 ← v₃''=0 (solid line), and to v₃'=0 ← v₃''=1 (dotted line). The four electronic states are labeled as in Figure 3.1.

Table 3-3 Spectroscopic constants, dissociation energies and equilibrium bond lengths for the ground and excited states of $\text{Co}^+(\text{H}_2\text{O})$. Term values T_{00} , excited state frequencies ν_3 and anharmonicities x_3 for the Co-O stretch are determined from the photodissociation spectrum.

The values in parentheses are assigned by extrapolating the spectra. Morse dissociation energies D_0 are calculated using equation 3-2 with the experimental frequencies and anharmonicities and corrected for zero-point energy. Experimental D_0 are calculated from dissociation to the Co^+ atomic state shown. The ground state frequency is calculated at the CCSD(T)/aug-cc-pVTZ level and the anharmonicity determined using the experimental dissociation energy.

State	$T_{00} (\text{cm}^{-1})$	$\nu_3 (\text{cm}^{-1})$	$x_3 (\text{cm}^{-1})$	$D_0 \text{ Morse} (\text{cm}^{-1})$	$r_e (\text{\AA})$	Co^+ State	$D_0 \text{ Experiment} (\text{cm}^{-1})$
X	0	400	2.9	-	1.97	$^3\text{F}_4$	13730±90
A	(13505)	318.2	3.2	7900	2.16±0.02	$^3\text{F}_3$	10930
B	(13640)	330.7	3.3	8100	2.16±0.02	$^3\text{F}_4$	9900
C	15872	328.4	1.7	15700	2.16±0.02	$^3\text{P}_1$	11259
D	16048	329.0	2.6	10200	2.11±0.03	$^3\text{P}_2$	10940

The lowest energy at which $\text{Co}^+(\text{H}_2\text{O})$ photodissociates is the $(\nu_3'=1, K_a'=0) \leftarrow (\nu_3''=0, K_a''=1)$ transition of band **A** at 13808 cm^{-1} . This gives an upper limit to the $\text{Co}^+-\text{H}_2\text{O}$ bond strength (corrected for the rotational energy in $K_a''=1$, approximately 8 cm^{-1}) of $D_0(\text{Co}^+-\text{H}_2\text{O}) \leq 13816 \text{ cm}^{-1}$. Transitions to $\nu_3'=0$ are not observed for bands **A** and **B**, implying that these transitions lie below the dissociation energy. The bond strength's lower limit is estimated from the observed $\nu_3'=1-5$ transitions in band **B**, extrapolated to $\nu_3'=0$ at 13640 cm^{-1} . Combining the upper and lower limits gives $D_0(0 \text{ K})(\text{Co}^+-\text{H}_2\text{O}) = 13730 \pm 90 \text{ cm}^{-1} = 164.2 \pm 1.1 \text{ kJ/mol}$. This is more precise than, and in agreement with, the values reported earlier: $155 \pm 12 \text{ kJ/mol}$,² $168 \pm 16 \text{ kJ/mol}$ ³ and $161 \pm 7 \text{ kJ/mol}$.⁴

The relative intensities in each ν_3' vibrational progression reflect the change in the Co-O bond length following electronic excitation. These intensities are the product of the absorption and photodissociation cross sections. Unlike $\text{TiO}^+(\text{CO}_2)$, where the fragment time-of-flight spectrum shows clear tailing due to photodissociation on the microsecond timescale and

competition with fluorescence,⁵⁰ no such tailing is observed for $\text{Co}^+(\text{H}_2\text{O})$, indicating that photodissociation occurs in <100 ns. The fluorescence lifetime is estimated to be at least 4 μs , based on the calculated integrated oscillator strength, $f=0.0010$. So, photodissociation is at least 40x faster than fluorescence. This indicates that the photodissociation quantum yield is near 1 throughout the spectrum. Thus, the analysis assumes that the photodissociation cross section is constant across the spectrum, so the intensities in the photodissociation spectrum mirror those in an absorption spectrum. These intensities are calculated by solving the one-dimensional Schrödinger Equation along the Co-O stretch coordinate. The molecule is treated as a pseudo diatomic, with the H_2O as a single “atom” with mass 18 amu. To determine $\Delta r_{\text{Co-O}}$ from the experimental intensities, the ground electronic state is modeled as a Morse oscillator with the CCSD(T) vibrational frequency and experimental dissociation energy. For each excited state, a Morse oscillator with the experimental frequency and anharmonicity is used, and $\Delta r_{\text{Co-O}}$ is adjusted until the best match is found between the calculated and measured intensities. This corresponds to a change in the metal-ligand bond length $\Delta r_{\text{Co-O}}$ of 0.14 to 0.19 Å, depending on the excited state. Although this analysis does not identify the sign of $\Delta r_{\text{Co-O}}$, it is clear from the rotational structure (discussed below) that the bond length increases upon electronic excitation.

The excited states of $\text{Co}^+(\text{H}_2\text{O})$ accessed in this study correlate to electronically excited $\text{Co}^{+*} + \text{H}_2\text{O}$. The excited states involved are identified by estimating the diabatic dissociation energy of each excited state. Treating the $\text{Co}^+ - \text{H}_2\text{O}$ stretch as a Morse oscillator,

$$D_e = \frac{\nu_3^2}{4 x_3} \quad 3-2$$

where ν_3 and x_3 are the Co-O stretching frequency and anharmonicity. The resulting values are shown in Table 3-3. The calculated dissociation energies have large uncertainties due to errors in fitting the diagonal anharmonicities, neglect of off-diagonal anharmonicities, and, most

importantly, in assuming that a Morse potential correctly describes the $\text{Co}^+ \text{-H}_2\text{O}$ interaction. It would be more accurate to determine the excited state dissociation limits using a LeRoy-Bernstein plot, properly accounting for the long-range $\text{Co}^+ \text{-H}_2\text{O}$ interactions. This approach has been used to measure very precise bond strengths for $\text{Co}^+ \text{-rare gas complexes}$.^{22,24,28} Unfortunately, this method is not applicable to $\text{Co}^+(\text{H}_2\text{O})$ as vibrational levels sufficiently close to the dissociation limit are not observed. The energy of the excited state of Co^+ is estimated using equation 3-3 and solving for $\Delta E(\text{Co}^{+*})$.

$$D'_0 = D''_0 + \Delta E(\text{Co}^{+*}) - T_{00} \quad 3-3$$

where D''_0 and D'_0 are dissociation energies for the ground and excited electronic state, $\Delta E(\text{Co}^{+*})$ is the energy difference between Co^+ and $(\text{Co}^+)^*$ and T_{00} is the origin band for the transition in the molecule. Using $D''_0 = 13730 \text{ cm}^{-1}$, the D'_0 values were calculated and are listed in Table 3-1. The resulting $\Delta E(\text{Co}^{+*})$ are sufficiently accurate to identify the triplet excited electronic state of Co^+ to which each excited state of $\text{Co}^+(\text{H}_2\text{O})$ correlates, but not the spin-orbit state. States **A** and **B** correlate to $\text{Co}^+ {}^3\text{F}_J (3\text{d}^7 4\text{s})$ at $9813\text{-}11322 \text{ cm}^{-1}$, while the **C** and **D** states correlate to ${}^3\text{P}_J (3\text{d}^8)$ at $13261\text{-}13593 \text{ cm}^{-1}$. If the parallel and perpendicular bands correspond to transitions from the ground state of $\text{Co}^+(\text{H}_2\text{O})$ (which correlates to the ${}^3\text{F}_4$ ground state of Co^+) to excited states with even ΔJ and odd ΔJ respectively, then we can assign the spin-orbit state to which each excited state correlates, and estimate D'_0 using equation 3-3, with the known $\Delta E(\text{Co}^{+*})$. These results are summarized in Table 3-3. Morse potential curves for the ground and excited states of $\text{Co}^+(\text{H}_2\text{O})$ observed in this study are shown Figure 3.4. The excited states are bound by $\sim 10000 \text{ cm}^{-1}$, or about 75% of the ground state binding energy. This is consistent with the observed decreased Co-O stretching frequency and increased Co-O bond length upon electronic excitation.

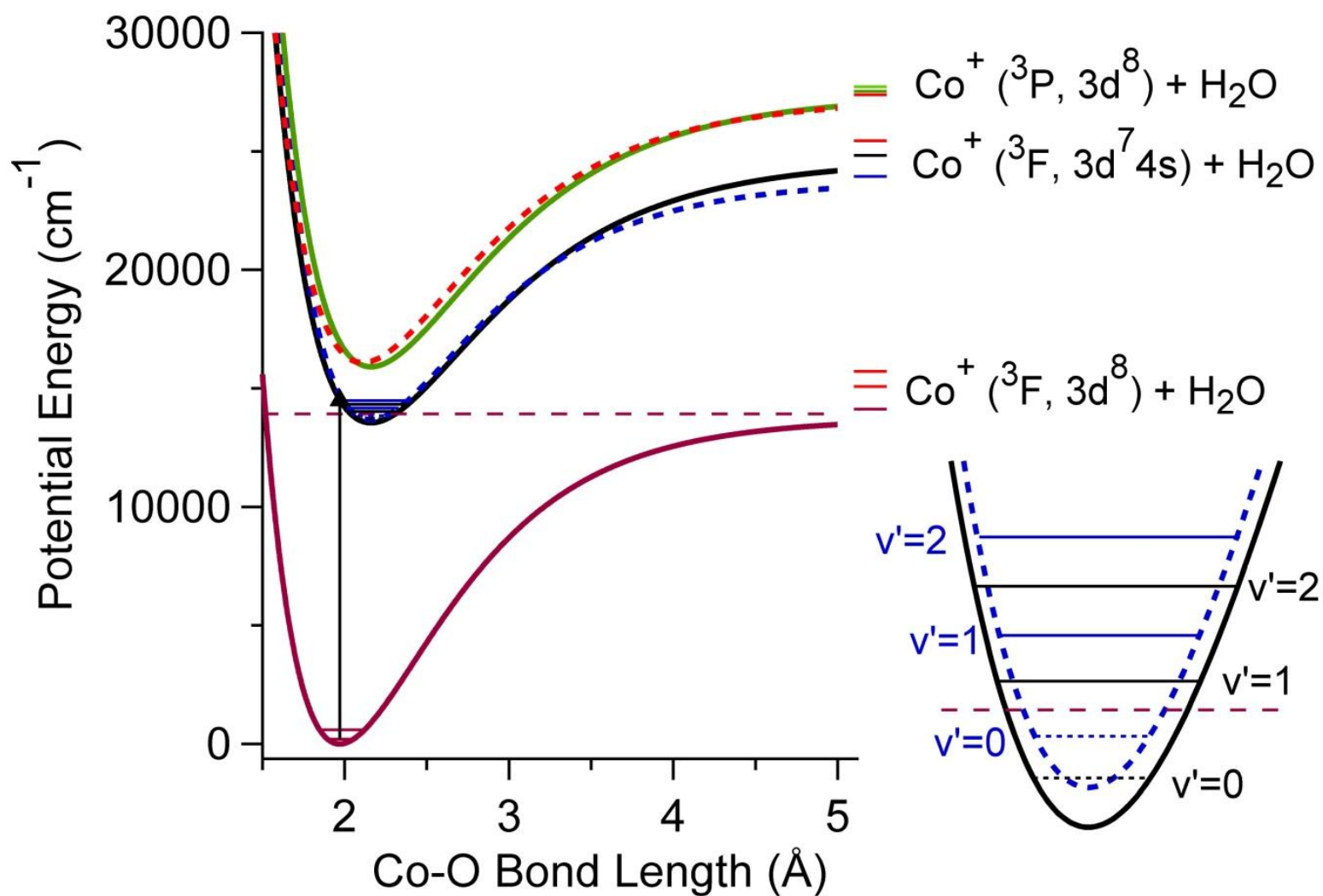


Figure 3.4 Potential energy curves of the ground and excited electronic states of $\text{Co}^+(\text{H}_2\text{O})$ along the Co-O stretch based on experiment. The inset shows an expanded view of the excited states in the region near the dissociation limit.

These results are similar to those observed in electronic photodissociation studies of $\text{Ni}^+(\text{H}_2\text{O})$ by our group and of $\text{Co}^+(\text{L})$ complexes by Brucat, Duncan and coworkers. In the $\text{Ni}^+(\text{H}_2\text{O})$ study, transitions from the $^2\text{A}_1$ ground state of $\text{Ni}^+(\text{H}_2\text{O})$, which correlates to the ^2D (3d^9) ground state of Ni^+ , to the nearly degenerate $^2\text{A}_1$ and $^2\text{A}_2$ excited states, which correlate to the $^2\text{F}_j$ ($3\text{d}^84\text{s}$) excited states of Ni^+ are observed.¹⁷ Each band contains a long progression in the Ni-O stretch, as the Ni-O bond lengthens by 0.20 Å upon electronic excitation. The diabatic bond strength of the excited states is also ~78% that of the ground state. The electronic spectra of $\text{Co}^+(\text{L})$ ($\text{L}=\text{Ne}$,²⁸ Ar ,^{22,23} Kr , Xe ,²⁴ CO_2 ^{25,26} and N_2 ²⁷) all show transitions to excited states in the visible with extended progressions in the Co-L stretch. The observed excited states correlate to $\text{Co}^+ ^3\text{F}_j$ ($3\text{d}^74\text{s}$) and $^3\text{P}_j$ (3d^8). In addition, Brucat and coworkers observed weak transitions to singlet states which correlate to $\text{Co}^+ ^1\text{D}_2$ (3d^8).²⁴ For many $\text{Co}^+(\text{RG})$ complexes, vibrational structure is observed up to the diabatic dissociation limit, which allows for the determination of very accurate bond strengths. The $\text{Co}^+\text{-RG}$ bond strengths range from 930 cm^{-1} for $\text{Co}^+(\text{Ne})$ to 7700 cm^{-1} for $\text{Co}^+(\text{Xe})$. Diabatic binding energies of excited states which correlate to 3d^8 states are smaller than those of the ground state, while those of states which correlate to $3\text{d}^74\text{s}$ states are even smaller. These photodissociation spectra typically show well-resolved rotational structure, from which bond lengths have been determined.

Time-dependent density functional theory calculations were implemented in order to characterize the electronic excitations which lead to the observed excited states of $\text{Co}^+(\text{H}_2\text{O})$. These calculations used the BHandHLYP functional with the 6-311++G(3df,p) basis set. This particular functional was selected because it predicts excitation energies of bare M^+ much more accurately than other popular functionals (e.g., B3LYP), as discussed in detail in our studies of $\text{V}^+(\text{OCO})$ and $\text{Ni}^+(\text{H}_2\text{O})$.^{17,51} Potential curves of the ground and excited triplet states of $\text{Co}^+(\text{H}_2\text{O})$ are shown in Figure 3.5. At each value of $r_{\text{Co-O}}$ the geometry of the rest of the molecule is fixed at

its equilibrium value. Several excited states are predicted in the energy range observed in the photodissociation spectrum. All of the bands in this region are calculated to be weak, with integrated oscillator strengths of $f < 0.0010$. This is consistent with the low signal levels observed.

Band **A** is likely due to the $2\ ^3A_2 \leftarrow X, \ ^3B_1$ transition, which is predicted to be a perpendicular band, with a calculated $T_e = 11700\text{ cm}^{-1}$. The primary excitation is $4b_1, 3d\pi \leftarrow 1a_2, 3d\delta$. Band **B** is tentatively assigned to the $2\ ^3B_2 \leftarrow X, \ ^3B_1$ transition ($4b_1, 3d\pi \leftarrow 4b_2, 3d\pi$), with a calculated $T_e = 12000\text{ cm}^{-1}$. Although this transition is symmetry forbidden, it could be observed due to vibronic coupling and/or to a magnetic dipole transition and is expected to show parallel band structure. This is observed in the $1A_2 \leftarrow X, \ ^1A_1$ band of H_2CS .⁵² Band **C** is assigned to the perpendicular $3\ ^3A_2 \leftarrow X, \ ^3B_1$ transition ($11a_1, 4s\sigma \leftarrow 4b_2, 3d\pi$), with a calculated $T_e = 16700\text{ cm}^{-1}$.

Band **D** is likely due to the $3\ ^3B_1 \leftarrow X, \ ^3B_1$ (primarily $11a_1, 4s\sigma \leftarrow 9a_1, 3d\delta + 3d\sigma$) transition, with a calculated $T_e = 14400\text{ cm}^{-1}$, although the symmetry forbidden $3\ ^3B_2 \leftarrow X, \ ^3B_1$ (primarily $11a_1, 4s\sigma \leftarrow 1a_2, 3d\delta$) transition, with a calculated $T_e = 16500\text{ cm}^{-1}$ is also a possibility.

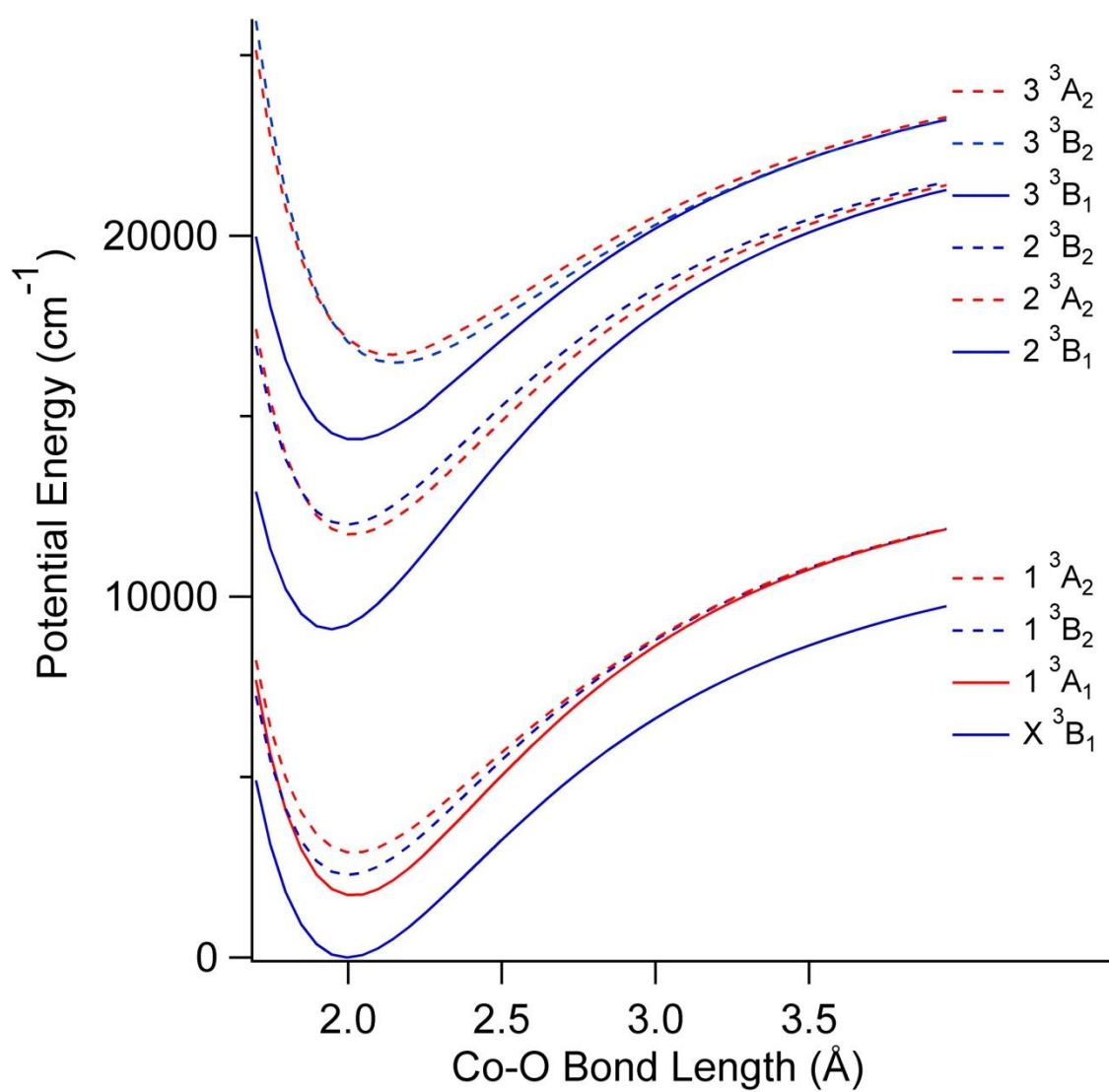


Figure 3.5 Potential energy curves for triplet states of $\text{Co}^+(\text{H}_2\text{O})$ along the Co-O stretch. Excited states are calculated using TD-DFT at the BHandHLYP/6-311++G(3df,p) level.

3.3.2 Electronic Spectroscopy: Rotational Structure

Rotational structure in the electronic transitions can give information about the geometry of the molecule, as well as the symmetry of the ground and excited states. As previously mentioned, the four electronic bands of $\text{Co}^+(\text{H}_2\text{O})$ show two types of rotational structure. Each vibrational transition in bands **A** and **C** (Figure 3.1) is a multiplet, consisting of several peaks spaced by about 30 cm^{-1} . This spacing is significantly smaller in $\text{Co}^+(\text{HOD})$ and even smaller in $\text{Co}^+(\text{D}_2\text{O})$. Bands **B** and **D** consist of single, sharp vibrational peaks. Analogous structure is also observed in electronic bands of $\text{M}^+(\text{H}_2\text{O})$ ($\text{M}=\text{Mg}$,⁸⁻¹⁰ Ca ,^{11,12} Ni ,¹⁷ Zn ¹⁸). For $\text{Ni}^+(\text{H}_2\text{O})$, the A'' and $B'' \approx C''$ rotational constants are approximately 13.8 cm^{-1} and 0.30 cm^{-1} , respectively,¹⁷ and similar values are expected for $\text{Co}^+(\text{H}_2\text{O})$. The rotational Hamiltonian for open-shell $\text{M}^+(\text{H}_2\text{O})$ can be expressed as the sum of a purely rotational and a spin-rotation term:^{53,54}

$$\mathbf{H} = \mathbf{H}_{rot} + \mathbf{H}_{sr} \quad 3-4$$

with

$$\mathbf{H}_{rot} = A\mathbf{N}_a^2 + B\mathbf{N}_b^2 + C\mathbf{N}_c^2 \quad 3-5$$

$$\mathbf{H}_{sr} = \frac{1}{2} \sum_{\alpha=a,b,c} \sum_{\beta=a,b,c} \epsilon_{\alpha,\beta} (\mathbf{N}_\alpha \mathbf{S}_\beta + \mathbf{S}_\beta \mathbf{N}_\alpha) \quad 3-6$$

where $\mathbf{N}$ is the rotational angular momentum, $\mathbf{S}$ is the spin angular momentum, A , B , and C are the rotational constants, and $\epsilon_{\alpha,\beta}$ are the components of the spin-rotation tensor in the inertial axis system (a, b, c). For a prolate near-symmetric top, the eigenvalues of $\mathbf{H}_{rot}$ are given by

$$E(J, K_a) = (A - \bar{B})K_a^2 + \bar{B}J(J+1) \quad 3-7$$

where J is the total rotational angular momentum quantum number, K_a is the quantum number for rotation along the a axis (the Co-O bond in our molecule), and $\bar{B} = \frac{1}{2}(B + C)$. For a symmetric prolate top, $A > B$ and $B=C$. The A rotational constant is inversely proportional to the

moment of inertia for rotation about the a axis. It thus depends on the H-O-H bond angle and the O-H bond length and is strongly affected by deuterium substitution. The multiplet bands (**A** and **C**) are perpendicular transitions with selection rules $\Delta K_a = \pm 1$ and $\Delta J = 0, \pm 1$.⁵⁵ The triplets observed for $\text{Co}^+(\text{H}_2\text{O})$ are due to transitions from $K_a''=0$ to $K_a'=1$ and from $K_a''=1$ to $K_a'=0$ and 2. The sharp bands **B** and **D** are parallel transitions with selection rules $\Delta K_a = 0$ and $\Delta J = 0, \pm 1$ for $K_a \neq 0$ and $\Delta K_a = 0$ and $\Delta J = \pm 1$ for $K_a = 0$. Transitions are observed from $K_a''=0$ to $K_a'=0$ and from $K_a''=1$ to $K_a'=1$. These transitions overlap as the A constants are similar for the two electronic states, resulting in a single peak rather than a multiplet. Because individual J lines are not resolved in the photodissociation spectra of $\text{Co}^+(\text{H}_2\text{O})$ and its isotopomers, the perpendicular transitions are more useful for determining rotational constants.

Figure 3.6 shows the $v_3'=2 \leftarrow v_3''=0$ transition in the perpendicular band **C** for $\text{Co}^+(\text{H}_2\text{O})$, $\text{Co}^+(\text{HOD})$ and $\text{Co}^+(\text{D}_2\text{O})$, highlighting the partially resolved rotational structure. The three major peaks are labeled by their K_a quantum numbers. Spin-rotation and J interaction determines the structure within each peak.

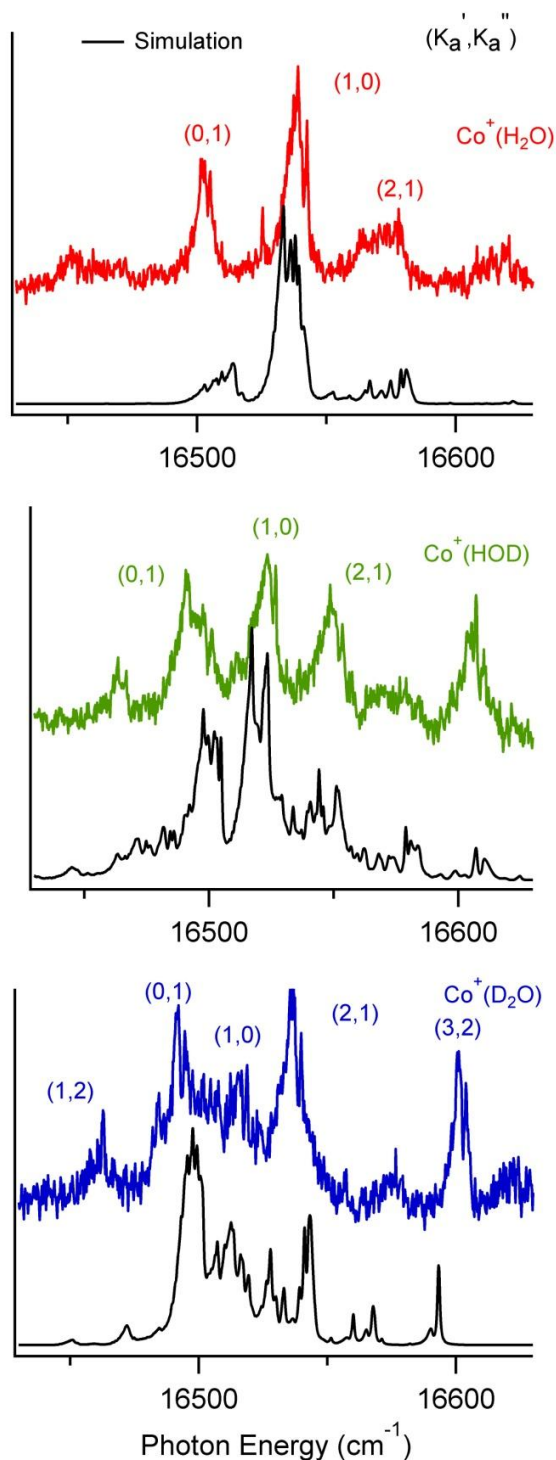


Figure 3.6 Partially resolved rotational spectra of the Band C ($v_3'=2 \leftarrow X^3B_1(v_3''=0)$) band of $\text{Co}^+(\text{H}_2\text{O})$ (top), $\text{Co}^+(\text{HOD})$ (middle) and $\text{Co}^+(\text{D}_2\text{O})$ (bottom) showing the $\Delta K_a=\pm 1$ features characteristic of a perpendicular transition. The simulated spectra are also shown, using the spectroscopic parameters in Table 3-4, a rotational temperature of 15 K and a Lorentzian linewidth of 1 cm^{-1} .

The relative intensities of peaks arising from $K_a''=0$ and 1 allow one to ascertain the lower state of the electronic transitions. These intensities are determined by the overall wavefunction, a product of vibrational, rotational, electronic and nuclear wavefunctions:

$$\Psi_{\text{tot}} = \Psi_{\text{vib}} \Psi_{\text{rot}} \Psi_{\text{elec}} \Psi_{\text{nuc}} \quad 3-8$$

where Ψ_{tot} must be ODD to satisfy conservation principles. The vibrational wavefunction Ψ_{vib} is EVEN for the ground state and for any a_1 vibration. The rotational wavefunction Ψ_{rot} is EVEN if K_a'' is even, and ODD if K_a'' is odd. At ~15 Kelvin, $\text{Co}^+(\text{H}_2\text{O})$ molecules cool to $K_a''=0$ and 1. Cooling states with $K_a''=1$ to $K_a''=0$ is very inefficient, as it requires changing nuclear spin. If $\text{Co}^+(\text{H}_2\text{O})$ has C_{2v} symmetry, the two protons are equivalent, and there are 3 symmetric (EVEN) states in Ψ_{nuc} and 1 antisymmetric (ODD) state. For $\text{Co}^+(\text{D}_2\text{O})$, the EVEN:ODD ratio is 1:2. Thus, if Ψ_{elec} is EVEN, the spectra should show enhanced intensity for odd K_a'' for $\text{Co}^+(\text{H}_2\text{O})$ and for even K_a'' for $\text{Co}^+(\text{D}_2\text{O})$. This is what is observed in electronic spectra of $\text{M}^+(\text{H}_2\text{O})$ ($\text{M}=\text{Mg}$,⁸⁻¹⁰ Ca ,^{11,12} Ni ,¹⁷ Zn ¹⁸), all of which have $^2A_1$ ground states. However, the spectra in Figure 3.6 show enhanced intensity for $K_a''=0$ for $\text{Co}^+(\text{H}_2\text{O})$ and for $K_a''=1$ for $\text{Co}^+(\text{D}_2\text{O})$, indicating that states with $K_a''=0$ have ODD overall spatial symmetry. This same intensity pattern is observed in the perpendicular bands **A** and **C**. In the parallel bands, transitions from $K_a''=0$ and 1 overlap, making intensity comparisons difficult. In C_{2v} symmetry, the electronic wavefunction is symmetrical (EVEN) for rotation about the C_2 axis (the a axis) for states with A symmetry and is antisymmetrical (ODD) for states with B symmetry. The observed intensities indicate that the lower state involved has Ψ_{elec} ODD and thus has B_1 or B_2 symmetry. Calculations predict that the ground state of $\text{Co}^+(\text{H}_2\text{O})$ is $^3B_1$ or $^3A_2$ (Table 3-1), with a low-lying $^3A_1$ state. The $^3B_2$ state is somewhat higher in energy and is often calculated to distort to C_s symmetry. Thus, based on the calculations and experimental intensities, $\text{Co}^+(\text{H}_2\text{O})$ has C_{2v} symmetry and the lower electronic state in the perpendicular transitions is a $^3B_1$ state. This state is identified as the ground state of $\text{Co}^+(\text{H}_2\text{O})$, as the relative

intensities of bands **A-D** do not depend on the conditions in the ion source (and hence its temperature).

The rotational structure in the spectra of $\text{Co}^+(\text{H}_2\text{O})$, $\text{Co}^+(\text{HOD})$ and $\text{Co}^+(\text{D}_2\text{O})$ was simulated using the *spfit* and *spsat* programs.⁵⁶ Figure 3.6 shows simulated spectra, and the fit parameters are listed in Table 3-4. Fits to the spectra indicate a Lorentzian linewidth of 1 cm^{-1} , which likely reflects the excited state lifetime. Spectra obtained over a range of photodissociation laser fluences show the same relative peak intensities and widths, indicating negligible power broadening. The modest spectral resolution precludes detailed analysis of the J structure. In addition, although the spin-rotation interaction parameter, ϵ , has components along all three rotational axes, ϵ_{aa} will dominate as the A rotational constant is much larger than $B \approx C$. Therefore, in the analysis, all other components of ϵ are assumed to be zero. To further constrain the fits, the ground state rotational constants are set to their calculated values. Based on the calculated CCSD(T)/aug-cc-pVTZ ground state geometry, $\text{Co}^+(\text{H}_2\text{O})$ is a near-prolate top with rotational constants $A_e''=13.93\text{ cm}^{-1}$, $B_e''=0.292\text{ cm}^{-1}$ and $C_e''=0.286\text{ cm}^{-1}$. To correct these rotational constants for zero-point displacement, an anharmonic frequency calculation was carried out. Because this is not available for CCSD(T) in *Gaussian09*, the computations were carried out at the BHandHLYP/6-311++G(3df,p) level, and the difference between the zero-point corrected and equilibrium rotational constants is added to the CCSD(T) equilibrium rotational constants, giving $A_0''=13.74\text{ cm}^{-1}$, $B_0''=0.289\text{ cm}^{-1}$ and $C_0''=0.283\text{ cm}^{-1}$. The simulations are moderately sensitive to changes in B and C on electronic excitation, and clearly indicate that the Co-O bond lengthens ($\Delta B < 0$). Due to the modest spectral resolution, $\Delta r_{\text{Co-O}}$ determined from the vibrational intensities is substantially more precise than $\Delta r_{\text{Co-O}}$ derived from rotational analysis of ΔB . The vibrational analysis gives $\Delta r_{\text{Co-O}}=0.19 \pm 0.02\text{ \AA}$. For $\text{Co}^+(\text{H}_2\text{O})$, this implies $\Delta B = -0.044\text{ cm}^{-1}$ which is the value used in the fit. The rotational constants of

$\text{Co}^+(\text{HOD})$ and $\text{Co}^+(\text{D}_2\text{O})$ are obtained from those of $\text{Co}^+(\text{H}_2\text{O})$ by changing the appropriate masses, while conserving the geometry.

Two factors contribute to the spin-rotation parameter ϵ : coupling of the electron spin to the magnetic field due to molecular rotation and, the dominant factor, second-order interaction between spin-orbit coupling and the Coriolis interaction.⁵⁴ In isolated Co^+ , the spin-orbit splitting is 227 cm^{-1} for the $^3\text{F} (3\text{d}^8)$ ground state, 214 cm^{-1} for the $^3\text{F} (3\text{d}^8 4\text{s}^1)$ excited state and 130 cm^{-1} for the $^3\text{P} (3\text{d}^8)$ excited state. The large atomic spin-orbit coupling leads to fairly large spin-rotation constants. Including the spin-rotational Hamiltonian modifies the energies given by equation 3-7. A perturbation treatment shows that it introduces an additional term proportional to $\epsilon_{aa} K_a \Sigma$, where $\Sigma=0, \pm 1$ is the projection of the spin angular momentum onto the a axis. This leads to broadening in peaks with $K_a > 0$. It also produces a term proportional to $\epsilon_{aa} K_a^2$, which affects the apparent A rotational constant.^{12,57} For $\text{Co}^+(\text{H}_2\text{O})$, we determine $\epsilon''_{aa} = -6 \text{ cm}^{-1}$. For comparison, in $\text{Ni}^+(\text{H}_2\text{O})$ $\epsilon''_{aa} = -12 \text{ cm}^{-1}$. The effect of this parameter is most clearly seen in the width of the $K_a' = 0 \leftarrow K_a'' = 1$ peak. For the upper state, $\epsilon'_{aa} = 4 \text{ cm}^{-1}$, which leads to the broad structure in the $K_a' = 2 \leftarrow K_a'' = 1$ peak. For $\text{Co}^+(\text{HOD})$ and $\text{Co}^+(\text{D}_2\text{O})$, ϵ''_{aa} and ϵ'_{aa} were optimized in the fit.

In the absence of spin-rotation interaction, equation 3-7 predicts that the $K_a' = 0 \leftarrow K_a'' = 1$ and $K_a' = 2 \leftarrow K_a'' = 1$ transitions are separated by $4A'$. As noted above, ϵ'_{aa} modifies this spacing. Once ϵ'_{aa} has been fit, A' can be determined. Excitation of the Co-O stretch ν_3' should reduce the B and C rotational constants, but should have little effect on the A rotational constant. This is confirmed by the anharmonic frequency calculations. However, comparison of the rotational structure of features in band **C** with $\nu_3' = 0$ to 5 shows that the spacing between the $K_a' = 0 \leftarrow K_a'' = 1$ and $K_a' = 2 \leftarrow K_a'' = 1$ peaks drops monotonically from 85 cm^{-1} for $\nu_3' = 0$ to 53 cm^{-1} for $\nu_3' = 5$ (Figure 3.7).

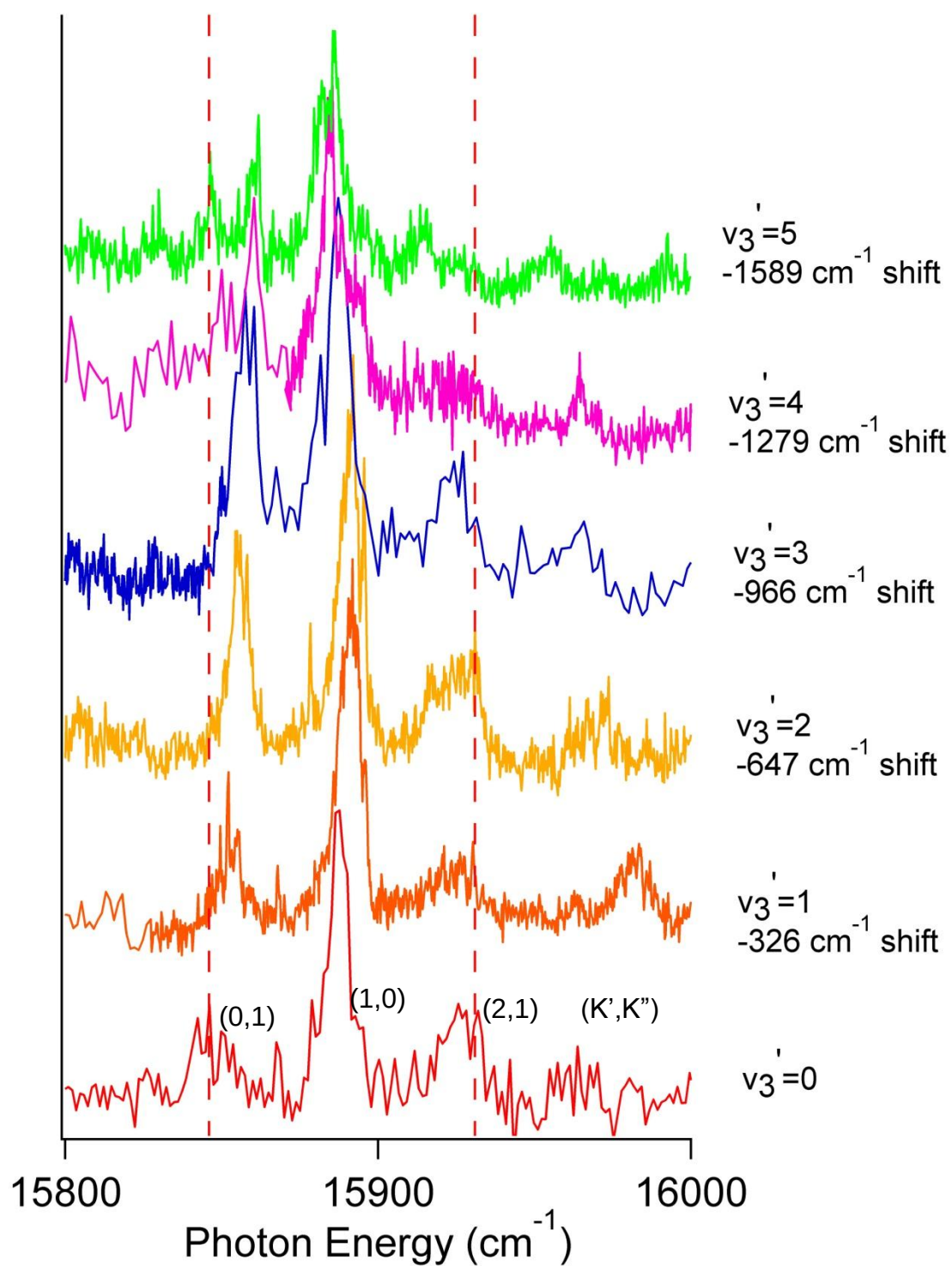


Figure 3.7 Overlapped photodissociation spectrum of $\text{Co}^+(\text{H}_2\text{O})$, highlighting the rotational structure in band C with $v_3' = 0$ to 5. The spacing between the (0,1) and (2,1) transitions drops with increasing Co-O stretch quantum number, which indicates a reduction in the excited state A' rotational constants.

Fitting the spectra thus requires unphysically large values of $A' \approx 21 \text{ cm}^{-1}$ for $v_3' = 0$ and rather low $A' \approx 13 \text{ cm}^{-1}$ for $v_3' = 5$. The rotational structure in bands **A** and **B** is even more strongly perturbed than that in bands **C** and **D**. Band **A** shows reduction of A' with increased Co-O stretch, and, unlike band **C**, exhibits a change in the relative intensities of the K_a features. With increasing Co-O stretch excitation, band **B** shows a small amount of perpendicular rotational structure. This is not observed in band **D**. The rotational structure in these bands is clearly perturbed. These perturbations also preclude obtaining better fits than those shown in Figure 3.6. The primary perturbation mechanism is likely to be rotations coupling nearby electronic states via Coriolis interaction. The **A** and **B** states are almost degenerate, as are the **C** and **D** states. Interactions between these states could lead to perturbations in the rotational structure that depend strongly on the excitation energy. In addition, direct vibronic coupling between these states is also possible. Spin-orbit interactions can couple the excited triplet states of $\text{Co}^+(\text{H}_2\text{O})$ to quintet states and to the singlet state of $\text{Co}^+(\text{H}_2\text{O})$, which correlate to $\text{Co}^+ (^5F_J$ at $3351\text{-}5205 \text{ cm}^{-1}$) and $\text{Co}^+ (^1D_2$ at 11651 cm^{-1}), respectively. As a result of these perturbations, the upper-state rotational constants derived from fitting the spectra are not physically meaningful and cannot be used to determine the excited state geometry. In principle, meaningful rotational constants could be determined from a deperturbation analysis. A proper deperturbation analysis requires a spectrum with well-resolved J and K_a structure. Unfortunately, as a result of the short excited-state lifetime, J structure is not resolved.

3.3.3 Vibrational Spectroscopy

A key question is how the presence of the metal ion affects the bonding in the water ligand. One way to address this question is to measure the vibrations of the ligand. Our calculations predict that binding to Co^+ reduces the water O-H stretching frequencies by $\sim 50 \text{ cm}^{-1}$.

¹ for the symmetric stretch, $\sim 80\text{ cm}^{-1}$ for the antisymmetric stretch, and $\sim 20\text{ cm}^{-1}$ for the bend (Table 3-2). Comparable red shifts in the O-H stretches have been observed in other transition metal $M^+(H_2O)$ complexes.^{17,29-37}

Measuring vibrational spectra of small, tightly-bound ions using photodissociation is challenging. Breaking the strong Co^+-H_2O bond requires four photons in the O-H stretching region. This high bond strength and the small size of the molecule make infrared multiple-photon dissociation (IRMPD) very inefficient. Spectra of several $M^+(H_2O)$ have been measured via photodissociation of argon-tagged $M^+(H_2O)(Ar)_n$ complexes, where absorption of light by the O-H chromophore eventually leads to loss of the weakly bound argon.²⁹⁻³⁷ Calculations predict that the presence of the argon usually only leads to small shifts in the O-H stretching frequencies. However, the argon does change the rotational structure. A particular concern in $Co^+(H_2O)$ is that the energies of the $^3B_1$, $^3A_1$ and $^3A_2$ states are so similar that binding to argon could actually change the ground state! Because $Co^+(H_2O)$ has a structured electronic photodissociation spectrum, vibrationally mediated photodissociation (VMP) is used to measure its vibrational spectrum. In this two laser double-resonance technique, parent molecules are dissociated at a fixed wavelength in the visible region while an infrared laser, firing 30 ns earlier, scans through the wavelength region of interest. When the IR laser is in resonance with a vibrational transition, molecules will be vibrationally excited, which leaves less population in the ground vibrational level. As the photodissociation laser is set to a wavelength where vibrationally cold molecules absorb, but vibrationally excited molecules do not (or absorb only weakly), the vibrational excitation leads to less photodissociation. Hence a vibrational spectrum is obtained by monitoring the depletion or “dip” of the fragment signal. We have used this technique to measure the O-H stretching vibrations of $Ni^+(H_2O)$.¹⁷

Figure 3.8 shows vibrational spectra of $\text{Co}^+(\text{H}_2\text{O})$ in the O-H stretching region measured using VMP. The spectrum in the top panel was obtained with the photodissociation laser set to the 16215 cm^{-1} ($v_3'=1, K_a'=1$) $\leftarrow$ X^3B_1 ($v_3''=0, K_a''=0$) transition. This double-resonance experiment only probes vibrational transitions with $K_a''=0$. The first peak corresponds to the O-H symmetric stretch vibration v_1 , a parallel transition ($\Delta K_a=0$) where the (0,0) transition is observed at 3610 cm^{-1} . The second peak, the O-H antisymmetric stretch vibration v_5 , is a perpendicular transition ($\Delta K_a=\pm 1$); exciting the intense (1,0) transition at 3693 cm^{-1} leads to >40% depletion of the photofragment signal. Similar vibrational spectra are observed when exciting other electronic transitions with $K_a''=0$. The lower spectrum was obtained with the photodissociation laser set to the 16253 cm^{-1} ($v_3'=1, K_a'=2$) $\leftarrow$ X^3B_1 ($v_3''=0, K_a''=1$) transition. The observed transitions all have $K_a''=1$. The symmetric stretch (1,1) transition is also observed at 3610 cm^{-1} , while the antisymmetric stretch leads to two absorptions, (0,1) at 3670 cm^{-1} and (2,1) at 3713 cm^{-1} .

In principle, vibrational spectra can also be measured in an enhancement experiment in which the visible laser is set to a wavelength at which vibrationally excited molecules selectively absorb. We have used this method to measure vibrational spectra of $\text{V}^+(\text{OCO})$, with greatly improved signal-to-noise over the depletion experiment.⁵⁸ In order to find the absorption of the vibrationally excited molecules, the IR laser is first set to an absorption and the visible laser is scanned. The difference between the resulting spectrum and one with the IR laser blocked gives the photodissociation spectrum of vibrationally excited molecules. For small molecules such as $\text{V}^+(\text{OCO})$ this often has well-defined peaks. In the present study, the IR laser was set to 3693 cm^{-1} as the visible laser scanned the low-energy region of bands **A** and **B**. Unfortunately, the resulting vibrationally mediated photodissociation spectrum is broad, with no sharp features. This persists for other IR bands shown in Figure 3.8, and when scanning over bands **C** and **D** as

well. The vibrationally mediated photodissociation spectrum of $\text{Ni}^+(\text{H}_2\text{O})$ is also mostly non-resonant, although one moderately intense peak is observed.¹⁷ This indicates that the initially excited vibrational state is mixing during the ~ 30 ns interval between the two laser pulses. Two possible mechanisms are vibrational state mixing within the ground electronic state or mixing with other low-lying electronic states. For larger species, the vibrationally excited molecules often show a broad photodissociation spectrum due to efficient intramolecular vibrational relaxation (IVR).⁵⁹ However, IVR should be slow in a molecule as small as $\text{Co}^+(\text{H}_2\text{O})$ due to the low vibrational density of states near 3700 cm^{-1} . The observed state mixing thus occurs via coupling to one of the many low-lying electronic states; the $^3\text{A}_2$ and $^3\text{A}_1$ states are calculated to lie within 40 cm^{-1} of the $^3\text{B}_1$ ground state, and $^3\text{B}_2$ state is also low-lying. Rotations can couple these electronic states via Coriolis interaction.

The vibrational spectra were simulated using the *spfit* and *spcat* programs,⁵⁶ and the results are shown in Figure 3.8 and summarized in Table 3-4. The simulations use a temperature of 15 K and assume that the visible laser overlaps all of the thermally populated J states, so the double resonance experiment selects states with specific K_a'' but does not select J'' . For the ground state, the same calculated rotational constants are used as for the electronic spectrum. Anharmonic frequency calculations at the BHandHLYP level predict rotational constants for the ground and excited vibrational states. The change in rotational constants upon vibrational excitation ($\Delta A = -0.13\text{ cm}^{-1}$, $\Delta B = \Delta C = 0$ for ν_1 and ν_5) was then used in the spectral simulations. The spin-rotation parameter ϵ_{aa} was assumed to be the same for the ground and vibrationally excited states. For the ground electronic state, the previously determined $\epsilon_{aa} = -6 \pm 1\text{ cm}^{-1}$ gives a good fit to the vibrational and electronic spectra. The O-H symmetric stretch frequency is $\nu_1 = 3609.7 \pm 1\text{ cm}^{-1}$ and the O-H antisymmetric stretch is $\nu_5 = 3679.5 \pm 2\text{ cm}^{-1}$.

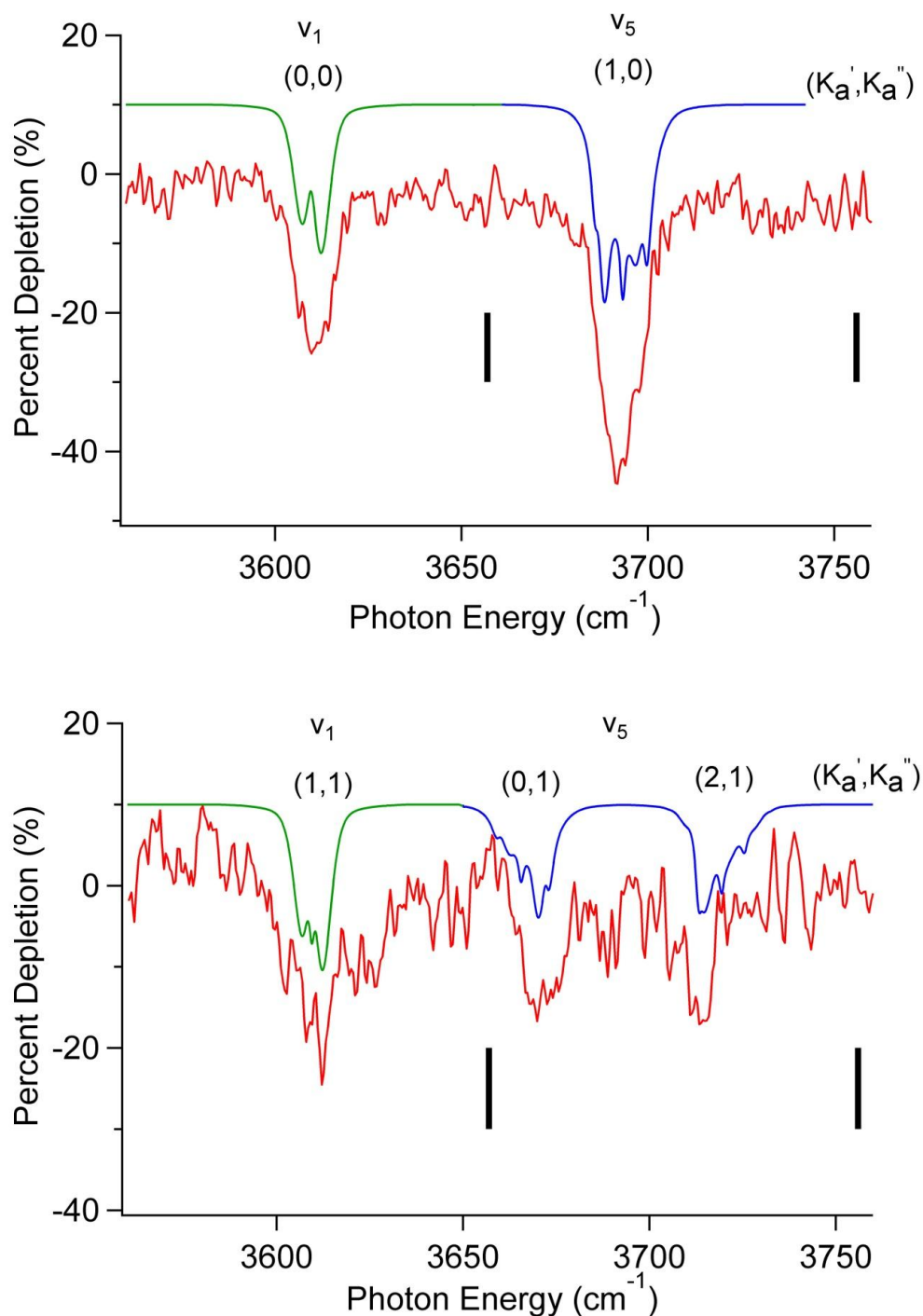


Figure 3.8 Vibrational spectra of $\text{Co}^+(\text{H}_2\text{O})$ in the O-H stretching region. The spectra are obtained by vibrationally mediated photodissociation, monitoring depletion in the Co^+ photofragment produced by irradiation of the $(v_3'=1, K_a'=1) \leftarrow X \text{ } ^3\text{B}_1 (v_3''=0, K_a''=0)$ transition at 16215 cm^{-1} (top) and $(v_3'=1, K_a'=2) \leftarrow X \text{ } ^3\text{B}_1 (v_3''=0, K_a''=1)$ transition at 16253 cm^{-1} (bottom). IR absorption removes molecules from $v''=0$, leading to a 15-45% reduction in the fragment yield. Simulated spectra are also shown, using the spectroscopic parameters in Table 3-4. Vertical bars denote the positions of the symmetric and antisymmetric stretches in bare H_2O .

Binding to Co^+ thus leads to red shifts of 47 and 76 cm^{-1} in the symmetric and antisymmetric stretching frequencies, respectively. For $\text{Co}^+(\text{HOD})$ we measure an O-H stretching frequency of 3650 cm^{-1} , a red shift of 57 cm^{-1} compared to bare HOD. The $\text{Co}^+(\text{HOD})$ vibrational spectrum and fit are in Figure 3.9. When Co^+ binds to H_2O , it removes electron density from the oxygen, which slightly weakens the O-H bonds. This leads to a red shift in the O-H stretching frequencies.

The red shifts are slightly larger than those observed in $\text{Ni}^+(\text{H}_2\text{O})$,¹⁷ 40 cm^{-1} and 68 cm^{-1} . Furukawa *et al.* measured IR spectra of $\text{Co}^+(\text{H}_2\text{O})_n$ ($n=4-6$) in the O-H stretching region via photodissociation spectroscopy.³⁹ Their spectra show that all the ions are three coordinate and are fairly hot, so the sharpest spectrum obtained is of the tagged cluster $\text{Co}^+(\text{H}_2\text{O})_4(\text{N}_2)$. This ion has IR absorptions at 3430 and 3530 cm^{-1} due to H-bonded OH groups and at 3620 and 3710 cm^{-1} due to free OH groups. The free-OH stretches are less red-shifted than in $\text{Co}^+(\text{H}_2\text{O})$, as each water molecule donates less electron density to the cation in the cluster.

Table 3-4 Rotational constants for $\text{Co}^+(\text{H}_2\text{O})$ and Isotopomers (cm^{-1}). Excited state values are for the $v_3'=2$ band of electronic state C. ^a) Calculated at the CCSD(T)/aug-cc-pVTZ level.

$\text{Co}^+(\text{H}_2\text{O})$	$^3\text{B}_1$ Ground State ($v''=0$)	State C ($v_3'=2$)
A	13.74^a	14.5
B	0.289^a	0.245
C	0.283^a	0.241
ϵ_{aa}	-6 ± 1	4 ± 1
$\text{Co}^+(\text{D}_2\text{O})$		
A	6.87^a	7.3
B	0.252^a	0.212
C	0.243^a	0.203
ϵ_{aa}	-3 ± 1	6 ± 1
$\text{Co}^+(\text{HOD})$		
A	9.56^a	9.95
B	0.272^a	0.228
C	0.264^a	0.224
ϵ_{aa}	-3.5 ± 1	3 ± 1

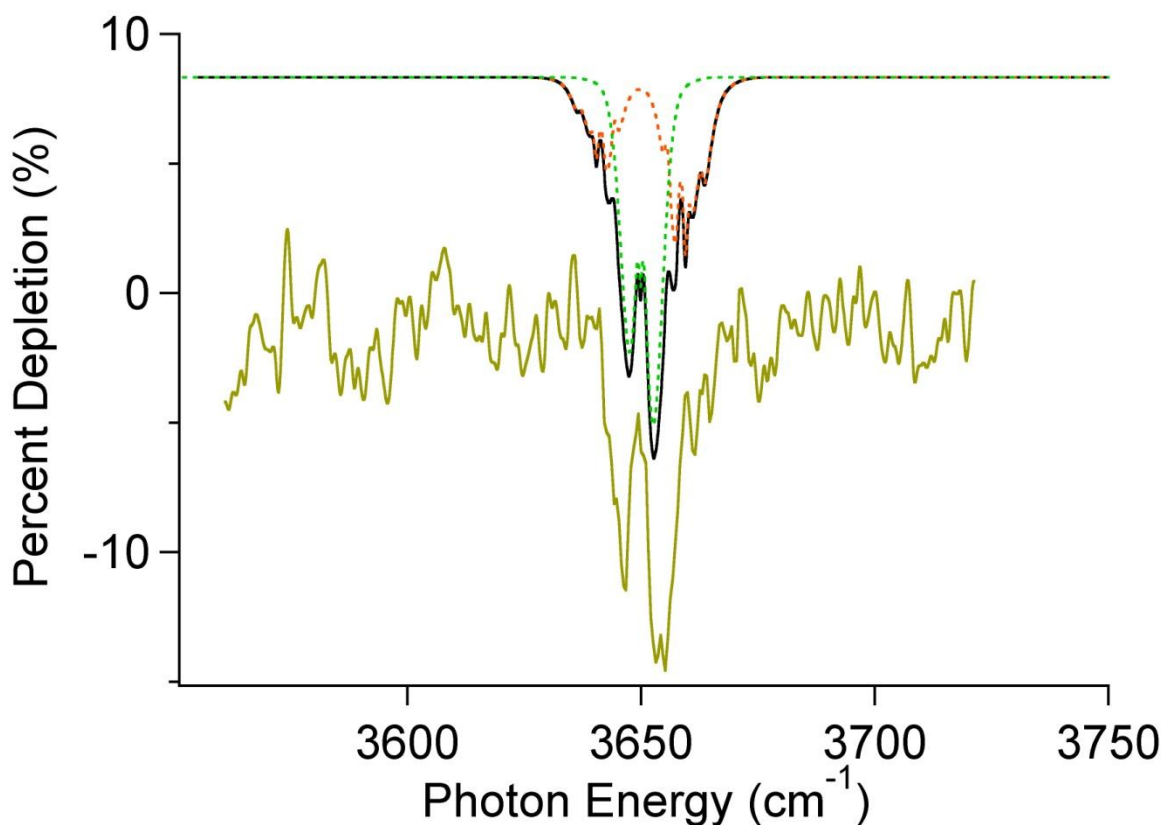


Figure 3.9 Vibrational spectrum of $\text{Co}^+(\text{HOD})$ in the O-H stretching region. The spectrum is obtained by vibrationally mediated photodissociation, monitoring depletion in the Co^+ photofragment produced by irradiation of the band $\text{C } (v_3'=4, K_a'=1) \leftarrow \text{X } ^3\text{B}_1 (v_3''=0, K_a''=0)$ transition at 17139 cm^{-1} . The simulated spectrum (shown in black) contains both parallel (shown in green) and perpendicular (shown in red) contributions. The simulation uses the following parameters, all in cm^{-1} : $\nu_0=3650$, $A''=9.56$, $B''=0.272$, $C''=0.264$, $\epsilon''_{aa}=-3.5$; $A'=9.46$, $B'=0.272$, $C'=0.264$, $\epsilon'_{aa}=-3.5$. Only ν_0 and $\epsilon''_{aa}=\epsilon'_{aa}$ are adjusted in the fit. Rotational constants A_e , B_e and C_e , from the CCSD(T)/aug-cc-pVTZ geometry, are corrected by the change in the rotational constant due to zero point (to get ground state constants) and to OH stretch excitation (to get upper state constants) using anharmonic frequency calculations at the BHandHLYP/6-311++G(3df,p) level.

3.4 Summary and Conclusions

The electronic spectra of $\text{Co}^+(\text{H}_2\text{O})$, $\text{Co}^+(\text{HOD})$ and $\text{Co}^+(\text{D}_2\text{O})$ were measured from 13500 cm^{-1} to 18400 cm^{-1} using photodissociation spectroscopy. They show transitions to four excited electronic states, with long progressions in the Co-O stretch and partially resolved rotational structure. The absolute vibrational quantum numbering is assigned by comparing isotopic shifts between $\text{Co}^+(\text{H}_2^{16}\text{O})$ and $\text{Co}^+(\text{H}_2^{18}\text{O})$. For the two low-lying excited electronic states, the first transition observed is to $v_3'=1$. This allows the $\text{Co}^+(\text{H}_2\text{O})$ binding energy to be bracketed as $D_0(0\text{ K}) (\text{Co}^+-\text{H}_2\text{O})=13730\pm90\text{ cm}^{-1}$ ($164.2\pm1.1\text{ kJ/mol}$). The ground state is assigned as $^3\text{B}_1$ based on the nuclear spin statistics of the K_a rotational structure. The vibrational spectrum of $\text{Co}^+(\text{H}_2\text{O})$ in the O-H stretching region was measured using vibrationally mediated photodissociation. The O-H stretches are observed at $\nu_1=3609.7\text{ cm}^{-1}$ for the symmetric stretch and $\nu_5=3679.5\text{ cm}^{-1}$ for the antisymmetric stretch. This corresponds to a 47 cm^{-1} red shift for the symmetric stretch and 76 cm^{-1} red shift for the antisymmetric stretch, relative to free H_2O .

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CHAPTER 4

VIBRATIONAL SPECTROSCOPY OF $\text{Co}^+(\text{CH}_4)_n$ AND $\text{Ni}^+(\text{CH}_4)_n$ ($n=1-4$)

4.1 Introduction

As discussed in Chapter 1, direct, efficient conversion of methane to a liquid such as larger hydrocarbons or methanol has been a long-standing goal of catalysis.¹ The indirect process first reacts methane with steam to produce synthesis gas (steam reforming, which is endothermic and inefficient), followed by the Fischer-Tropsch process, catalyzed by iron and cobalt, to produce liquid hydrocarbons. Nickel is widely used as a catalyst for steam reforming, which is also the primary process for industrial hydrogen production. The catalytic importance of these reactions has also prompted extensive fundamental studies of methane activation on nickel surfaces^{2,3} and by gas-phase metal atoms and ions.⁴⁻¹¹

The binding of methane to M^+ includes electrostatic and covalent contributions. The strength of the interaction depends on the electronic configuration of the metal. In particular, those with a $3d^n 4s^0$ ground state (such as Co^+ and Ni^+) interact more strongly with ligands than those with $3d^{n-1} 4s^1$ (such as Mn^+). This is because the 3d orbitals are smaller than the 4s and they are directional, so they can orient to minimize repulsion with ligands.

Previous spectroscopic studies of $\text{M}^+(\text{CH}_4)_n$ complexes include the electronic spectra of $\text{Mg}^+(\text{CH}_4)$,¹² $\text{Ca}^+(\text{CH}_4)$,¹³ $\text{V}^+(\text{CH}_4)$ ¹⁴ and $\text{Zn}^+(\text{CH}_4)$ ¹⁵ and vibrational spectroscopy of $\text{Li}^+(\text{CH}_4)_{1-6}$,^{16,17} $\text{Al}^+(\text{CH}_4)_{1-6}$,¹⁸ $\text{Mn}^+(\text{CH}_4)_{1-6}$ ¹⁹ and $\text{Fe}^+(\text{CH}_4)_{1-4}$.²⁰

Computations carried out in conjunction with the thermodynamic measurements of Zhang *et al.*^{21,22} predict that many of the clusters have several potential isomers with similar energies. In these cases, the binding energy measurements cannot determine the most stable structure. Vibrational spectroscopy of the C-H stretches is complementary, as it is sensitive to the ligand coordination (η^2 vs. η^3) and the metal-ligand distance. In this study, we report

vibrational spectroscopy of $\text{Co}^+(\text{CH}_4)_{1-4}$ and $\text{Ni}^+(\text{CH}_4)_{1-4}$ measured via photofragment spectroscopy. Experimental results are compared to calculated spectra of candidate structures to identify the geometry of the complexes.

4.2 Experimental and Computational Methods

The $\text{M}^+(\text{CH}_4)_n$ ($\text{M}=\text{Co}, \text{Ni}$; $n=1-4$) clusters are generated in an expansion gas mixture of methane in helium at ~ 50 psi backing pressure. Mixes containing $\sim 0.1-1\%$ methane are used to produce $n=1, 2$ clusters, and more concentrated mixes with $\sim 5\%$ methane are used for larger clusters ($n=3, 4$). The photodissociation spectrum is obtained by taking the ratio of fragment to parent signal and normalizing to laser power as a function of laser wavelength. For these vibrational spectroscopy studies, a wavelength range of $2500-3300\text{ cm}^{-1}$ was scanned with an Nd:YAG pumped OPO/OPA laser. This produces approximately 5 mJ per pulse near 3000 cm^{-1} , with a line width of 1.8 cm^{-1} . The IR laser is calibrated using the absorption spectrum of methane gas.²³

The $\text{Co}^+(\text{CH}_4)_n$ and $\text{Ni}^+(\text{CH}_4)_n$ clusters with $n=1, 2$ have dissociation energies of $>7500\text{ cm}^{-1}$, so photodissociation requires absorption of more than one photon. To measure spectra of these molecules, two techniques were investigated. The first method, infrared multiple-photon dissociation spectroscopy (IRMPD), was previously used to measure spectra of $\text{Fe}^+(\text{CH}_4)_n$ ($n=1, 2$).²⁰ Unfortunately, IRMPD of $\text{Co}^+(\text{CH}_4)_n$ and $\text{Ni}^+(\text{CH}_4)_n$ leads to no dissociation for $n=1$ and to very low dissociation and broad peaks for $n=2$. Thus a second method, argon-tagging,²⁴⁻²⁸ was used to measure the spectra for $n=1, 2$. Because it binds weakly, absorption of one IR photon by cluster ions with Ar attached leads to dissociation by loss of Ar. Argon-tagging also ensures that parent ions are vibrationally cold. As a result, the spectrum is generally sharp and has a high photodissociation yield. On the other hand, the tag may affect the metal-methane binding,

shifting the vibrational frequencies. This effect is assessed by comparing the calculated spectra of tagged and un-tagged molecules.

Calculations were carried out using the B3LYP hybrid density functional with the 6-311++G(3df,3pd) basis set²⁹ using the Gaussian 09 program package.³⁰ Systematically varying the basis set from 6-311+G(d,p) to 6-311++G(3df,3pd) leads to only a 4 cm⁻¹ maximum shift in the C-H stretching frequencies, but predicts slightly higher methane binding energies. Additional calculations were carried out using the long-range corrected CAM-B3LYP functional.³¹ This consistently predicts higher binding energies.

The calculated B3LYP/6-311++G(3df,3pd) frequencies are scaled by a variable scaling factor. The physical justification is that C-H vibrations are not harmonic and the anharmonicity is greater for C-H stretches of hydrogens that are towards the metal (proximate). The C-H stretches of proximate hydrogens have larger red shifts than those of hydrogens pointing away from the metal (distal). Rizzo and co-workers have discussed a similar case where they used a scaling factor for N-H and C-H stretches which depends on the peak width, as hydrogen bonding leads to broader peaks, red-shifts, and larger anharmonicity.³² For our molecules, a linear scaling factor was used, with parameters determined by matching calculated and experimental spectra of M⁺(CH₄)_n(Ar)_{3-n} and M = Co, Ni; n=1,2. The resulting scaling factor (Equation 4-1) is used for all the spectra.

$$\text{Scaling factor} = 0.959 - 7.33 \times 10^{-5} \times (3131 \text{ cm}^{-1} - \nu) \quad 4-1$$

where ν is the un-scaled calculated frequency of each C-H stretch, and 3131 cm⁻¹ is the calculated antisymmetric C-H stretch frequency in bare CH₄. The scaling factor ranges from 0.93 to 0.96 for the spectral region shown in this work. Simulated spectra using the CAM-B3LYP functional (with scaling factors derived as above) are nearly identical to those obtained with B3LYP.

4.3 Results and Discussion

Vibrational spectroscopy is an ideal tool to investigate these non-covalent interactions, as binding to the metal leads to a substantial red shift in the proximate C–H stretching frequencies and increases their intensity. In particular, the C-H stretches of proximate hydrogens are very sensitive to the number of H atoms coordinated on each methane (η^1 , η^2 or η^3) and to the metal-carbon distance.

Vibrational spectra of $M^+(\text{CH}_4)_n$ and $M^+(\text{CH}_4)_m(\text{Ar})_{3-m}$ ($M = \text{Co, Ni}$; $n=3,4$; $m=1,2$) in the C-H stretching region measured using photofragment spectroscopy are shown in Figure 4.1. The experimental peak positions and their relative intensities are presented in Table 4-2. The spectra of smaller clusters with $m=1$ and 2 have intense peaks in the 2550-2600 cm^{-1} region. This corresponds to a 300-400 cm^{-1} red shift from the symmetric stretch in isolated CH_4 (2917 cm^{-1}). There are also weak features near the antisymmetric C-H stretch in isolated CH_4 (3019 cm^{-1}). The spectra of the larger clusters ($n=3$ and 4) are generally more complex and show smaller red shifts. For the larger clusters, the spectrum depends on the cluster size and the metal; they also differ from the spectra of manganese¹⁹ and iron²⁰ complexes. The spectra for each cluster will be discussed in detail and assigned in the next section.

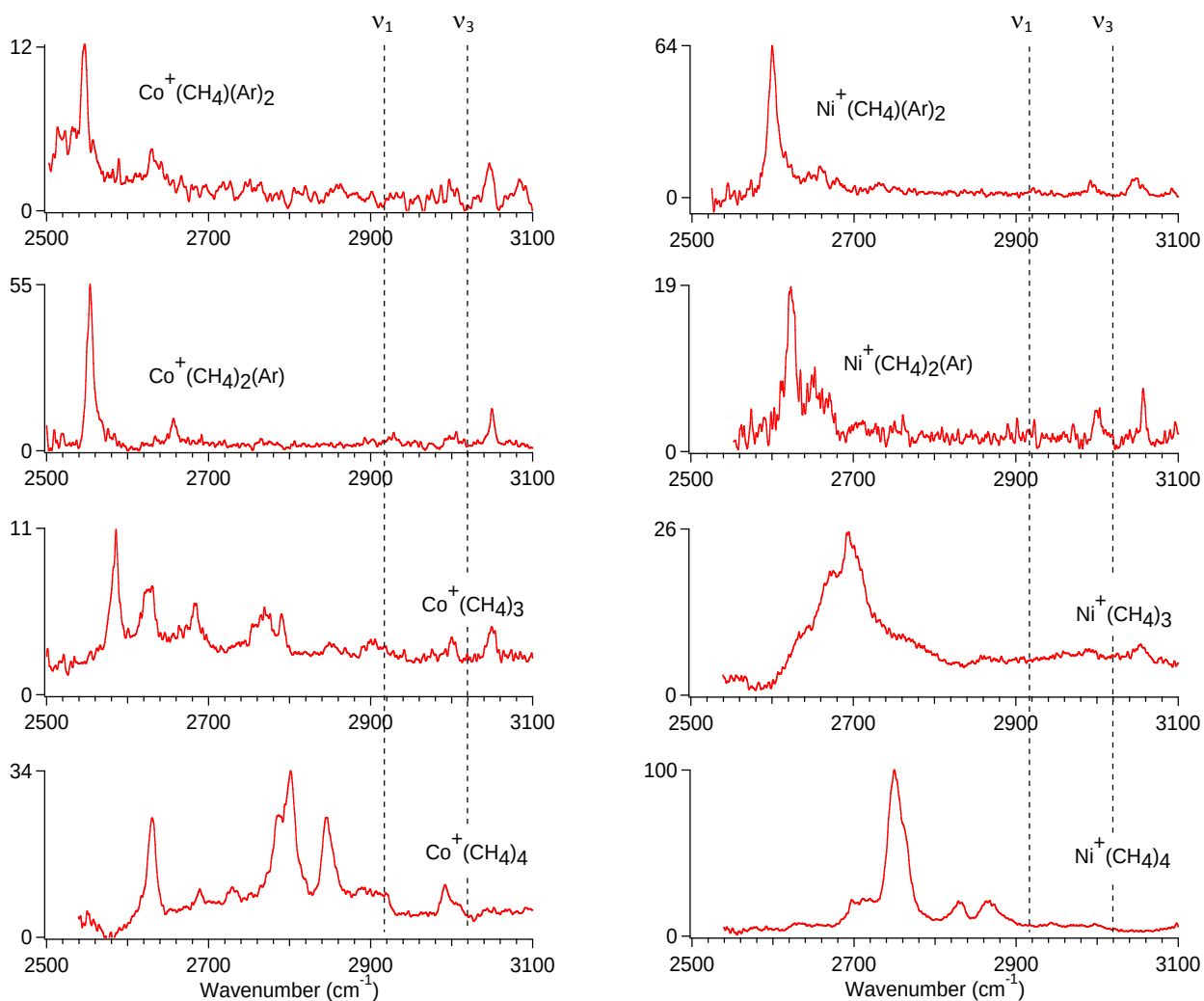


Figure 4.1 Experimental IR photodissociation spectra of $M^+(\text{CH}_4)(\text{Ar})_2$, $M^+(\text{CH}_4)_2(\text{Ar})$, and $M^+(\text{CH}_4)_n$ ($n=3,4$) in the C-H stretching region (2500-3100 cm^{-1}) for $M=\text{Co}$ (left column) and $M=\text{Ni}$ (right column). The dashed vertical lines show the isolated CH_4 symmetric ($\nu_1=2917 \text{ cm}^{-1}$) and antisymmetric ($\nu_3=3019 \text{ cm}^{-1}$) stretches. The y axis shows the normalized photofragment yield (relative to the 2749 cm^{-1} band in $\text{Ni}^+(\text{CH}_4)_4$.)

4.3.1 Bare and Ar-tagged $M^+(\text{CH}_4)$

Using IRMPD, no photodissociation was observed for $\text{Co}^+(\text{CH}_4)$ or $\text{Ni}^+(\text{CH}_4)$, whereas in our previous study²⁰ the spectrum of $\text{Fe}^+(\text{CH}_4)$ was obtained by IRMPD. This is not surprising, as the Co^+-CH_4 and Ni^+-CH_4 binding energies, measured by guided ion beam^{33,34} and equilibrium^{21,22,35} methods, are $>7500\text{ cm}^{-1}$ (Table 4-1), while the Fe^+-CH_4 binding energy is measured^{21,36} to be only $4760\pm250\text{ cm}^{-1}$ and 6120 cm^{-1} . Moreover, no dissociation was observed for $\text{Co}^+(\text{CH}_4)(\text{Ar})$ and $\text{Ni}^+(\text{CH}_4)(\text{Ar})$. This is due to their high argon binding energies, calculated to be 3771 and 4087 cm^{-1} , respectively (see below for details). This is similar to the Co^+-Ar and Ni^+-Ar binding energies, which have been measured^{37,38} to be $4111\pm5\text{ cm}^{-1}$ and $4572\pm5\text{ cm}^{-1}$, respectively.

Figure 4.2 shows the photodissociation spectra of $\text{Co}^+(\text{CH}_4)(\text{Ar})_2$ and $\text{Ni}^+(\text{CH}_4)(\text{Ar})_2$ taken by monitoring Ar loss. The $\text{Co}^+(\text{CH}_4)(\text{Ar})_2$ spectrum consists of an intense peak at 2547 cm^{-1} , with weaker features at 2630 and 3046 cm^{-1} . This is characteristic of an η^2 methane complex. The two low-frequency vibrations are due to the symmetric and antisymmetric C-H stretches of the proximate hydrogens, respectively. The large red shift reflects weakening of these C-H bonds by the strong Co^+ -methane interaction. The weak high-frequency features are due to the symmetric and antisymmetric distal C-H stretches. These show little shift from the antisymmetric stretch in isolated CH_4 . The vibrational spectrum of $\text{Ni}^+(\text{CH}_4)(\text{Ar})_2$ is similar to that of the cobalt complex with the proximate C-H stretches at 2597 and 2657 cm^{-1} . This is a smaller red shift than is observed for $\text{Co}^+(\text{CH}_4)(\text{Ar})_2$. The distal C-H stretches are observed at 2992 and 3048 cm^{-1} . These spectra are qualitatively different from those of $M^+(\text{CH}_4)$ ($M=\text{Li}$,^{16,17} Al ,¹⁸ Mn ,¹⁹ and Fe ²⁰), which all have η^3 methane coordination.

Table 4-1 Experimental and Calculated 0 Kelvin Binding Energies (in cm^{-1}) of $\text{M}^+(\text{CH}_4)_{n-1}-\text{CH}_4$ and $\text{M}^+(\text{CH}_4)_n(\text{Ar})_{m-1}-\text{Ar}$ ($\text{M}=\text{Co}, \text{Ni}$; $n=1-4$; $m=1-2$). Calculated values are at the B3LYP/6-311++G(3df,3pd) level.

	M=Co			M=Ni		
	Experimental	Calculated ^e B3LYP	Calculated ^e CAM-B3LYP	Experimental	Calculated ^e B3LYP	Calculated ^e CAM-B3LYP
M^+-CH_4	$7500\pm500^{\text{a}}, 8080^{\text{b}}, 8010\pm250^{\text{c}}$	7927	8391	$8100\pm400^{\text{f}}, 8710\pm160^{\text{g}}$	8269	8734
$\text{M}^+(\text{CH}_4)-\text{Ar}$		3771	4181		4087	4542
$\text{M}^+(\text{CH}_4)(\text{Ar})-\text{Ar}$		1171	1540		1629	2024
$\text{M}^+(\text{CH}_4)-\text{CH}_4$	$8100\pm400^{\text{a}}, 8850^{\text{b}}, 8670\pm280^{\text{c}}$	7456	8121	9270^{g}	7712	8374
$\text{M}^+(\text{CH}_4)_2-\text{Ar}$		608	905		717	979
$\text{M}^+(\text{CH}_4)_2-\text{CH}_4$	$3300\pm400^{\text{a}}, 2550^{\text{b}}, 3850^{\text{cd}}, <2580^{\text{e}}$	1496	1977	$3250^{\text{g}}, <2670^{\text{e}}$	2495	2948
$\text{M}^+(\text{CH}_4)_3-\text{CH}_4$	$1820^{\text{b}}, <2631^{\text{e}}$	735	984	$1920^{\text{g}}, <2750^{\text{e}}$	1030	1460

^a Ref. ³³; ^b Ref. ³⁵; ^c Ref. ²²; ^d estimate; ^e this work; ^f Ref. ³⁴; ^g Ref. ²¹

Table 4-2 Experimental and predicted peak positions (cm^{-1}) and their relative intensities of Co^+ -methane and Ni^+ -methane complexes

	M=Co	M=Ni
$\text{M}^+(\text{CH}_4)$	2505*, 2578*, 3044*	2531**, 2601**, 2985**, 3047**
$\text{M}^+(\text{CH}_4)(\text{Ar})_2$	2547(s), 2630(w), 3046(w)	2597(s), 2657(w), 2992(w), 3048(w)
$\text{M}^+(\text{CH}_4)_2(\text{Ar})$	2554(s), 2657(w), 3049(m)	2623(s), 3001(w), 3057(w)
$\text{M}^+(\text{CH}_4)_2$	2532*, 2640*, 3049*	2640(m), 2965(m) 2544*, 2959*, 3067*
$\text{M}^+(\text{CH}_4)_3$	2586(s), 2627(m), 2682(m), 2769(m), 3000(w), 3049(w)	2633(w, sh), 2671(m, sh), 2694(s), 3054(w)
$\text{M}^+(\text{CH}_4)_4$	2631(s), 2785(m,sh), 2801(s), 2845(s), 2993(w)	2696(w, sh), 2749(s), 2831(w), 2867(w), 2943(vw), 2996(vw)

*=predicted, **=predicted for $^2\text{B}_1$ state, s=strong, m=medium, w=weak, vw=very weak, sh= shoulder

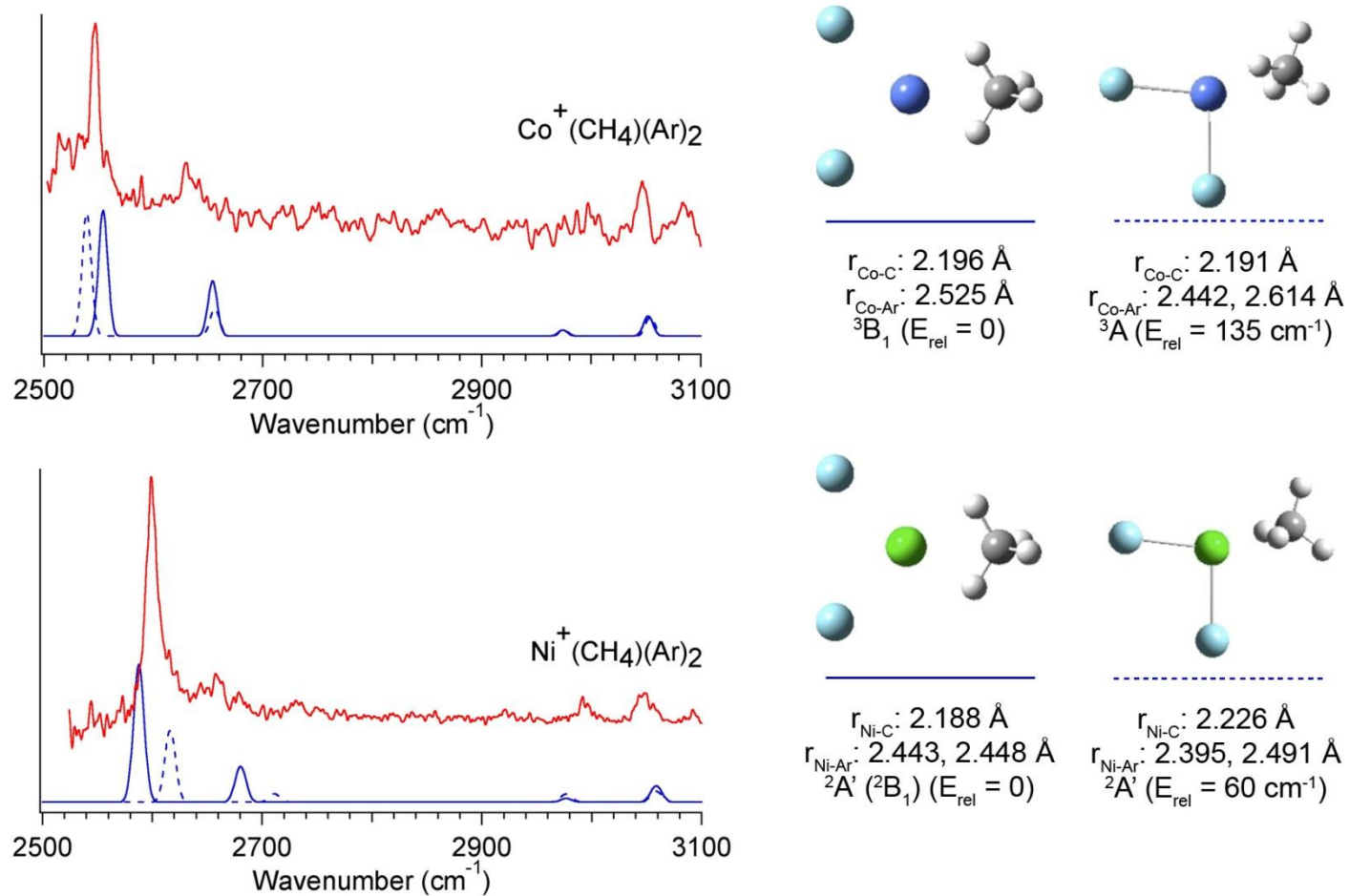


Figure 4.2 Experimental IR photodissociation spectra of $\text{M}^+(\text{CH}_4)(\text{Ar})_2$ ($\text{M}=\text{Co}, \text{Ni}$) (red), simulated spectra (blue), and calculated B3LYP/6-311++G(3df,3pd) structures.

Electronic structure calculations were used to further characterize the observed features and to elucidate the structure of the complexes. Goddard, Armentrout and coworkers calculated structures and binding energies of $\text{Co}^+(\text{CH}_4)_n$ ($n=1-4$) using the modified coupled pair functional (MCPF) method.^{33,39} Later, Bowers and co-workers calculated several possible geometries for the $\text{Co}^+(\text{CH}_4)_n$ and $\text{Ni}^+(\text{CH}_4)_n$ ($n=1-4$) complexes at the B3LYP level with the 6-311G(d,p) basis set for C, H and Wachters(f) basis set for the metal.^{21,22} Our calculations, which use the same functional and a larger, more flexible basis set, mostly agree with their results. The earlier studies did not use the current C_{2v} axis system. For consistency, all of their orbitals and states have been converted by reversing b_1 and b_2 .

For $\text{Co}^+(\text{CH}_4)$, our calculations predict that the molecule has C_{2v} symmetry and η^2 coordination with 2.159 Å Co-C bond length and a $^3B_1$ ground state. Energies, vibrational frequencies and intensities, structures, and Cartesian coordinates for calculated structures are given in Table 4-4. This is in a good agreement with results of Bowers and coworkers.²² They also identify an η^3 structure which is only 240 cm^{-1} higher in energy. We find that the η^3 structure relaxes to the η^2 ground state upon geometry optimization. We use a coordinate system in which the Co-C axis is the z axis and the proximate hydrogens are in the xz plane. The ground state of Co^+ is $^3F_4$ ($3d^8$). In $\text{Co}^+(\text{CH}_4)$, the Co^+ electronic configuration is

$$4b_2(d_{yz})^2 1a_2(d_{xy})^2 9a_1([d_{x^2-y^2} - d_{z^2}])^2 10a_1([d_{x^2-y^2} + d_{z^2}])^1 4b_1(d_{xz})^1 \quad 4-2$$

Figure 4.3 shows the molecular orbital diagram. This is the same orbital occupancy as is calculated for the $^3B_1$ ground state of $\text{Co}^+(\text{H}_2\text{O})$.⁴⁰ The $d_{x^2-y^2}$ and d_{z^2} orbitals, which have a_1 symmetry, mix extensively, giving rise to two orbitals. The $[d_{x^2-y^2} - d_{z^2}]$ term represents the combination of $d_{x^2-y^2}$ and d_{z^2} orbitals that form a $d_{x^2-z^2}$ -like orbital, which is doubly occupied, and $[d_{x^2-y^2} + d_{z^2}]$ represents the combination of these orbitals that forms a d_{y^2} -like orbital,

which is singly occupied. In the ideal case $d_{x^2-z^2} = \frac{1}{2} d_{x^2-y^2} - \frac{\sqrt{3}}{2} d_{z^2}$ (25% $d_{x^2-y^2}$ and 75% d_{z^2}) and $d_{y^2} = \frac{-\sqrt{3}}{2} d_{x^2-y^2} - \frac{1}{2} d_{z^2}$ (75% $d_{x^2-y^2}$ and 25% d_{z^2}). In $\text{Co}^+(\text{CH}_4)$, population analysis shows that the $9a_1$ orbital contains 14% $d_{x^2-y^2}$, 79% d_{z^2} and 7% $4s$; and the $10a_1$ orbital has 85% $d_{x^2-y^2}$, 12% d_{z^2} and 3% $4s$. The other singly occupied orbital, $4b_1(d_{xz})$, has the strongest interaction with the proximate C-H bonds. In this orbital, the methane acts as a π -donor. A NBO analysis shows $0.07e^-$ contribution from CH_4 to Co^+ ($0.05e^-$ from the a_1 orbitals and $0.02e^-$ from b_1). This interaction weakens the proximate C-H bonds. At the B3LYP/6-311++G(3df,3pd) level of theory the C-H bond length in bare CH_4 is 1.088 Å. Binding to Co^+ increases this by 0.035 Å for the proximate C-H bonds; the distal bond lengths are almost unchanged, decreasing by 0.002 Å. The calculated Co^+-CH_4 binding energy is 7927 cm^{-1} , in excellent agreement with experimental values (Table 4-1). Photodissociation thus requires at least three photons in the C-H stretching region. Therefore, vibrational spectra were measured via Ar-tagging and the structures of Ar-tagged complexes were also calculated.

In $\text{Co}^+(\text{CH}_4)(\text{Ar})$, the argon binds nearly opposite to the methane, forming a C_s complex with a calculated Ar-Co-C angle of 173° . Argon binding does not change the nature of the singly occupied orbitals in the complex. The calculated C-H stretching frequencies are slightly perturbed by the argon, shifting $2\text{-}10 \text{ cm}^{-1}$. The $\text{Co}^+(\text{CH}_4)\text{-Ar}$ bond strength is calculated to be 3771 cm^{-1} , which is still too high for one photon dissociation. This explains why no photodissociation was observed for $\text{Co}^+(\text{CH}_4)(\text{Ar})$. In $\text{Co}^+(\text{CH}_4)(\text{Ar})_2$ the second argon binds to the metal in a trigonal C_{2v} geometry, in which the argons and proximate hydrogens are in the same plane. The second argon does not change the electronic configuration of the complex. For the Ar_2 -tagged complex, the calculated C-H stretching frequencies of the proximate hydrogens are somewhat perturbed from those of $\text{Co}^+(\text{CH}_4)$, blue shifting by 42 and 51 cm^{-1} . The binding energy

of the second Ar is calculated to be 1171 cm^{-1} , which is well below the C-H stretching frequencies. The geometries of $\text{Co}^+(\text{CH}_4)(\text{Ar})_m$ ($m=0-2$) and calculated spectra are given in Figure 4.4. There are two higher-lying isomers of $\text{Co}^+(\text{CH}_4)(\text{Ar})_2$. These structures have the proximate hydrogens perpendicular to the plane of the heavy atoms. The first of these, lying 135 cm^{-1} above the ground state, has the CH_4 at one of the arms of a Tee. This isomer has a calculated spectrum very similar to that of the ground state, as shown in Figure 4.2. The second excited isomer (shown only in Table 4-4), at 538 cm^{-1} , is also Tee-shaped, but with the CH_4 at the base. Its calculated proximate C-H stretching frequencies are somewhat higher than those of the other states, and it doesn't contribute to the observed spectrum.

Figure 4.2 shows the photodissociation spectrum of $\text{Co}^+(\text{CH}_4)(\text{Ar})_2$. The observed high photofragment yield is consistent with a single photon dissociation process. The proximate C-H symmetric and antisymmetric stretching frequencies are 2547 cm^{-1} (strong) and 2630 cm^{-1} (weak), respectively. The spectrum also shows a weak distal C-H stretch at 3046 cm^{-1} . The calculated and scaled values for the ground state are 2537 and 2653 cm^{-1} for proximate and 2973 and 3052 cm^{-1} for distal C-H stretches. By adding the shift between the experimental and calculated C-H stretch frequencies in $\text{Co}^+(\text{CH}_4)(\text{Ar})_2$ to the calculated frequency of $\text{Co}^+(\text{CH}_4)$, it is possible to predict the C-H stretches of un-tagged $\text{Co}^+(\text{CH}_4)$. The proximate C-H stretching frequencies in $\text{Co}^+(\text{CH}_4)$ are predicted to be 2505 cm^{-1} (symmetric) and 2578 cm^{-1} (antisymmetric), which corresponds to shifts of 412 cm^{-1} and 339 cm^{-1} from the symmetric stretch of bare CH_4 , respectively. These large red shifts are characteristic of an η^2 structure. The distal C-H antisymmetric stretching frequency is predicted to be 3044 cm^{-1} . The distal C-H stretches are not affected by argon tagging.

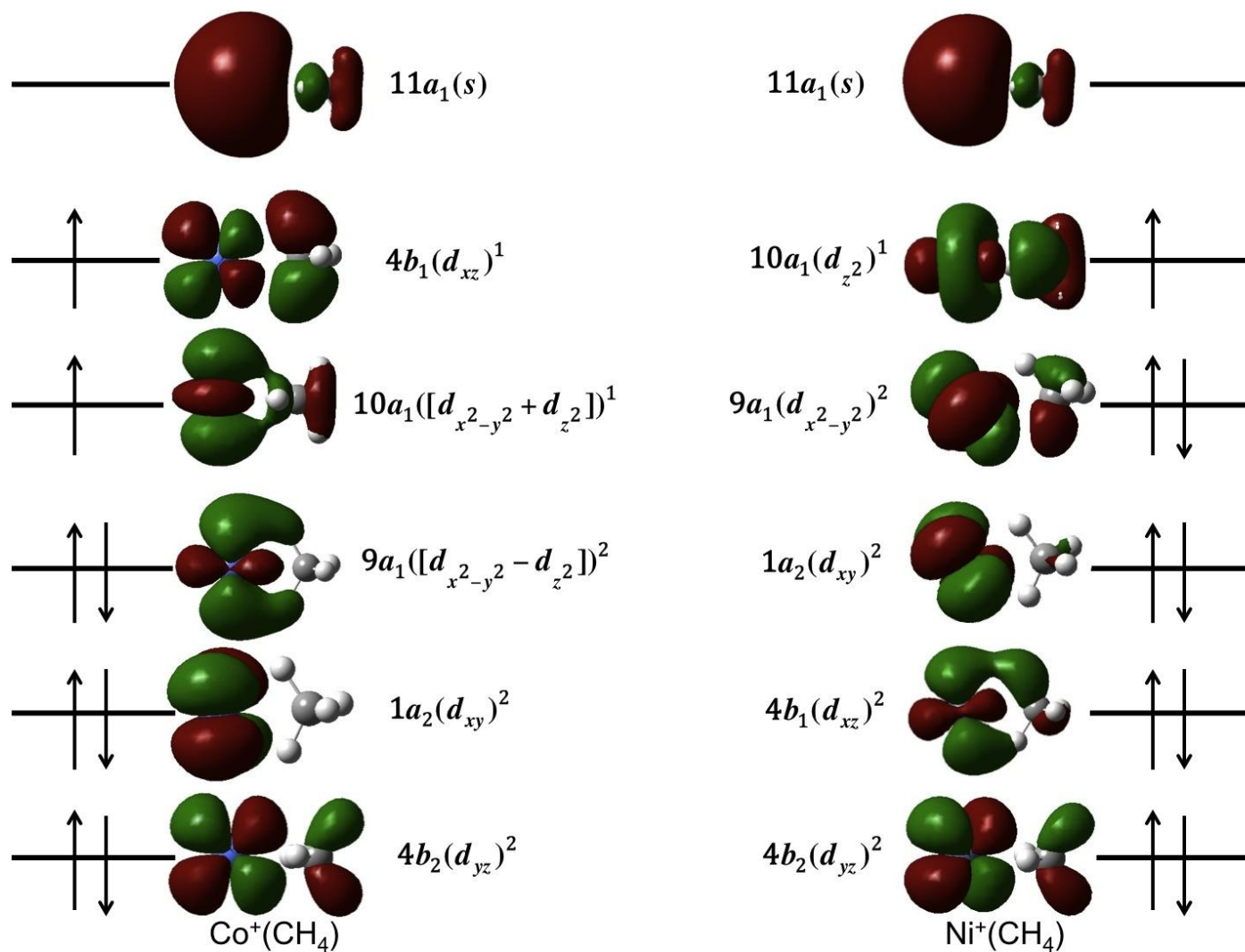


Figure 4.3 Molecular orbitals of $\text{Co}^+(\text{CH}_4)$ (left) and $\text{Ni}^+(\text{CH}_4)$ (right) from B3LYP/6-311++G(3df,3pd) calculations.

For $\text{Ni}^+(\text{CH}_4)$, our calculations predict that the molecule is slightly distorted from an η^2 , C_{2v} geometry. It has C_s symmetry and a $^2\text{A}'$ ground state (corresponding to $^2\text{A}_1$ in C_{2v}). The Ni-C bond length is 2.181 Å, while the Ni-proximate H distances are 1.823 Å and 1.959 Å. For ease of comparison, we will use C_{2v} labels for the C_s orbitals. As with $\text{Co}^+(\text{CH}_4)$, the Ni-C axis is the z axis; and the proximate hydrogens are in the xz plane. The ground state of Ni^+ is $^2\text{F}_{5/2}$ ($3d^9$). In $\text{Ni}^+(\text{CH}_4)$, the Ni^+ electronic configuration is

$$4b_2(d_{yz})^2 4b_1(d_{xz})^2 1a_2(d_{xy})^2 9a_1(d_{x^2-y^2})^2 10a_1(d_{z^2})^1 \quad 4-3$$

where a_1 and b_1 in C_{2v} become a' in C_s ; a_2 and b_2 become a'' . Figure 4.3 shows the molecular orbital diagram. This is the same orbital occupancy as is calculated for the $^2\text{A}_1$ ground state of $\text{Ni}^+(\text{H}_2\text{O})$.⁴¹ The singly occupied orbital, $10a_1(d_{z^2})$, has the strongest interaction with the proximate C-H bonds. In this orbital, similarly to the cobalt case, the methane acts as a π -donor. This interaction again weakens the proximate C-H bonds. Binding to Ni^+ increases the C-H bond length by 0.038 Å and 0.023 Å for the proximate C-H bonds; while the bond length for the distal ones decreases by 0.002 Å. The calculated binding energy of $\text{Ni}^+(\text{CH}_4)$ is 8269 cm^{-1} , in excellent agreement with experimental values (Table 4-1). Bowers and coworkers²² calculated a $\text{C}_{2v}(\text{x})$, $^2\text{B}_1$ ground state with the d_{xz} orbital singly occupied and a $\text{C}_{2v}(\text{z})$, $^2\text{A}_2$ state with d_{xy} singly occupied orbital 200 cm^{-1} higher in energy. With the larger basis set in our calculation, the $^2\text{B}_1$ state is an excited electronic state, lying only 160 cm^{-1} above the $^2\text{A}'$ ($^2\text{A}_1$) ground state, and has a Ni-C bond length of 2.148 Å. In C_s symmetry the $^2\text{A}_1$ and $^2\text{B}_1$ states would give a nearly degenerate pair of $^2\text{A}'$ states, which can mix, and this gives rise to our calculated ground state. We have also calculated a second $^2\text{A}_1$ and a $^2\text{A}_2$ excited state. These lie 350 cm^{-1} ($r_{\text{Ni-C}}=2.219 \text{ Å}$) and 712 cm^{-1} ($r_{\text{Ni-C}}=2.196 \text{ Å}$) above the $^2\text{A}'$ ground state, respectively.

For $\text{Ni}^+(\text{CH}_4)(\text{Ar})$, a C_s complex with an Ar-Ni-C angle of 169° is calculated. Argon binding does not change the electronic configuration of Ni^+ in the complex. The calculated C-H

stretching frequencies are slightly perturbed by the argon, shifting 1 to 29 cm^{-1} . The $\text{Ni}^+(\text{CH}_4)\text{-Ar}$ bond strength is predicted to be 4087 cm^{-1} , which is still too high for one photon dissociation. As noted above, in $\text{Ni}^+(\text{CH}_4)$, states with a hole in the d_{z^2} (often mixed with $d_{x^2-y^2}$) and d_{xz} are at similar energies. This behavior persists with argon tagging, and affects the geometry of the resulting complexes. In $\text{Ni}^+(\text{CH}_4)(\text{Ar})_2$, the metal is four coordinate. States with the d_{z^2} hole favor quasi-tetrahedral geometries, with the proximate hydrogens and argons staggered. Those with a d_{xz} hole are quasi-square planar, with the proximate hydrogens and argons eclipsed. As a result, in $\text{Ni}^+(\text{CH}_4)(\text{Ar})_2$, there are three distinct geometries with similar binding energies, similar to the situation for the analogous cobalt complex. The ground state is calculated to have a hole in the d_{xz} orbital, forming a nearly C_{2v} structure with a Ni-C bond length of 2.188 Å. The metal, proximate hydrogens and argons are all co-planar (eclipsed). In C_{2v} geometry this is a $^2\text{B}_1$ state, corresponding to the $\text{Ni}^+(\text{CH}_4)$ ground state calculated by Bowers and coworkers²², which was predicted to lie 160 cm^{-1} above the $^2\text{A}'$ state in our calculation. For $\text{Ni}^+(\text{CH}_4)(\text{Ar})_2$, the next state, at 60 cm^{-1} , is a C_s state with the d_{xz} doubly occupied. This is formed by taking $\text{Ni}^+(\text{CH}_4)(\text{Ar})$ and adding the second Ar in a Tee-shaped configuration, with an Ar-Ni-Ar angle of 98°. The Ni-C bond length is 2.226 Å and the Ni-H distances are much more symmetrical than in $\text{Ni}^+(\text{CH}_4)$, at 1.92 Å.

Addition of two argons to $\text{Ni}^+(\text{CH}_4)$ slightly weakens the metal-methane interaction, increasing the Ni-C bond length by ~ 0.03 Å, and increasing the frequency of the proximate C-H stretches by ~ 60 cm^{-1} and the distal C-H stretches by < 8 cm^{-1} . Figure 4.2 shows the experimental vibrational spectrum of $\text{Ni}^+(\text{CH}_4)(\text{Ar})_2$ along with scaled, simulated spectra of the $^2\text{B}_1$ and $^2\text{A}'$ states. The proximate C-H symmetric and antisymmetric stretching frequencies are 2597 cm^{-1} (strong) and 2657 cm^{-1} (weak), respectively. The spectrum also shows the distal C-H stretching frequencies at 2992 cm^{-1} (weak) and 3048 cm^{-1} (weak). The $^2\text{B}_1$ state is a slightly better match to

the experimental spectrum, with the proximate C-H symmetric stretch predicted to lie 11 cm^{-1} below the observed 2597 cm^{-1} , while the predicted value for the ${}^2A'$ state is 21 cm^{-1} too high. The ${}^2A_1$ state (not shown) is a poorer match, with a predicted value 42 cm^{-1} too high. This state is also predicted to lie 380 cm^{-1} above the ground state. Using the same approach as for cobalt, the proximate C-H stretching frequencies in the ${}^2B_1$ state of $\text{Ni}^+(\text{CH}_4)$ are predicted to be 2531 cm^{-1} (symmetric) and 2601 cm^{-1} (antisymmetric), which corresponds to shifts of 386 and 316 cm^{-1} from the symmetric stretch of bare CH_4 , respectively. Once again, these large red shifts are characteristic of an η^2 structure. The distal C-H stretching frequencies are predicted to be 2985 and 3047 cm^{-1} .

Vibrational spectra of $\text{Mn}^+(\text{CH}_4)$ and $\text{Fe}^+(\text{CH}_4)$ have been previously measured.^{19,20} Those experiments show that Mn^+ (${}^7S, 3d^5 4s^1$) and sextet Fe^+ (${}^6D, 3d^6 4s^1$) bind methane in η^3 coordination while Co^+ (${}^3F, 3d^8 4s^0$) and Ni^+ (${}^2D, 3d^9 4s^0$) bind in η^2 coordination. One would expect that the binding energies would be correlated with the red shifts in the lowest C-H stretching frequency of $\text{M}^+(\text{CH}_4)$ (compared to bare CH_4). The stronger the interaction between the metal and ligand, the larger the binding energy, the more electron density would flow from ligand to metal, and the weaker the proximate C-H bonds would become and the lower the vibrational frequencies would be. This idea holds in a broad sense but not in every single case. The interaction between the metal ion and ligand can be attributed to two main factors: electrostatics (ion-induced dipole attraction, e^-e^- repulsion) and covalency (σ and π donation and back donation). The $4s$ orbital is larger than the $3d$, so ions with the $4s$ occupied have smaller methane binding energies ($<34\text{ kJ/mol}$ ¹⁹ for Mn^+ and $\sim 40\text{ kJ/mol}$ for sextet Fe^+ (to sextet²⁰ $\text{Fe}^+(\text{CH}_4)$)) than those with the $4s$ empty ($95\pm 2\text{ kJ/mol}$ ²² or $90\pm 6\text{ kJ/mol}$ ⁴² for Co^+ ; $104\pm 2\text{ kJ/mol}$ ²¹ or $96\pm 5\text{ kJ/mol}$ ³⁴ for Ni^+). Ions with the $4s$ occupied such as Sc^+ , Ti^+ and Zn^+ are predicted to bind methane with η^3 coordination.^{15,43-46} The situation is more nuanced for those

with the 4s empty. Increasing the effective nuclear charge on the metal while filling the same (3d) orbital will increase the electrostatic attraction. This leads to the trend that early transition metal-methane complexes including V^+ , Cr^+ , Mn^+ and sextet Fe^+ are calculated to have η^3 coordination, while the late metals Co^+ , Ni^+ and Cu^+ tend to have η^2 coordination,^{19,21,22,33,34,39,44,47,48} with the crossover at quartet $Fe^+(CH_4)$, for which the η^2 structure is calculated to lie 50 cm^{-1} above the η^3 structure.²⁰ Binding to the metal leads to modest red shifts in the lowest C-H stretch of 81 cm^{-1} for $Mn^+(CH_4)$,¹⁹ and 104 cm^{-1} for sextet $Fe^+(CH_4)$.²⁰ The red shifts for the more strongly bound complexes are much larger: 271 cm^{-1} for quartet $Fe^+(CH_4)$,²⁰ 412 cm^{-1} for $Co^+(CH_4)$ (Table 4-2). For the latter two, recall that these are predicted values for the η^2 , C_{2v} complexes and that the red shift is sensitive to distortion from η^2 towards η^1 coordination. It is surprising that the red shift for the Co complex is larger than for the Ni complex, considering that the Ni complex is more strongly bound. This may be due to the fact that the d orbitals are directional, so it matters which d orbitals the electrons occupy. In the η^2 complexes the d_{z^2} and d_{xz} are the most repulsive as they point most directly towards the ligand. In $Co^+(CH_4)$ each of these orbitals is singly occupied, while in $Ni^+(CH_4)$ one must be doubly occupied. Therefore, $Co^+(CH_4)$ has the largest red shift.

4.3.2 Bare and Ar-tagged $M^+(CH_4)_2$

The $Co^+(CH_4)-CH_4$ and $Ni^+(CH_4)-CH_4$ binding energies, measured by guided ion beam³³ and equilibrium^{21,22,35} methods, are $>8100\text{ cm}^{-1}$ (Table 4-1). In each case, the second methane binds more strongly than the first. In contrast to $Co^+(CH_4)$ and $Ni^+(CH_4)$, where no IRMPD was observed, a small amount of dissociation ($\sim 0.5\%$) is seen for $Ni^+(CH_4)_2$. Despite its higher binding energy, its higher vibrational density of states likely contributes to more efficient IRMPD.

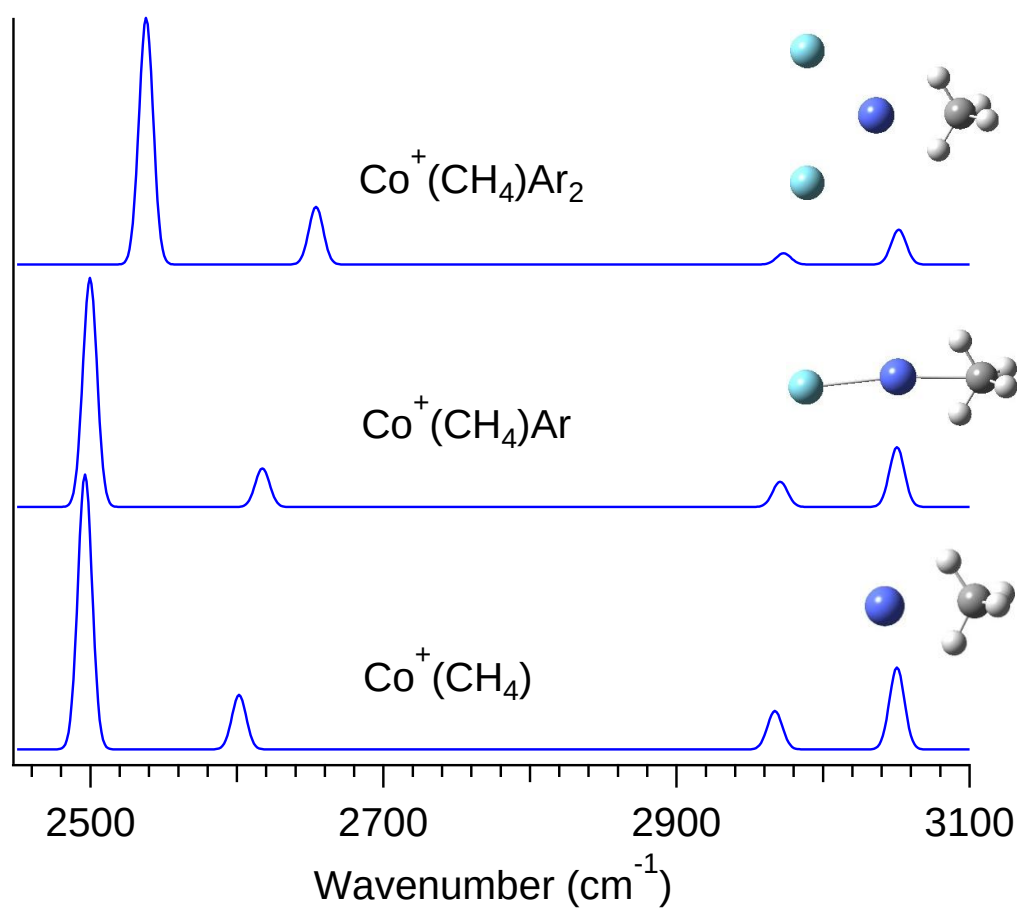


Figure 4.4 Calculated and scaled (equation 4-1) ground state structures and vibrational spectra for $\text{Co}^+(\text{CH}_4)(\text{Ar})_{0-2}$. Calculations are made at the B3LYP/6-311++G(3df,3pd) level.

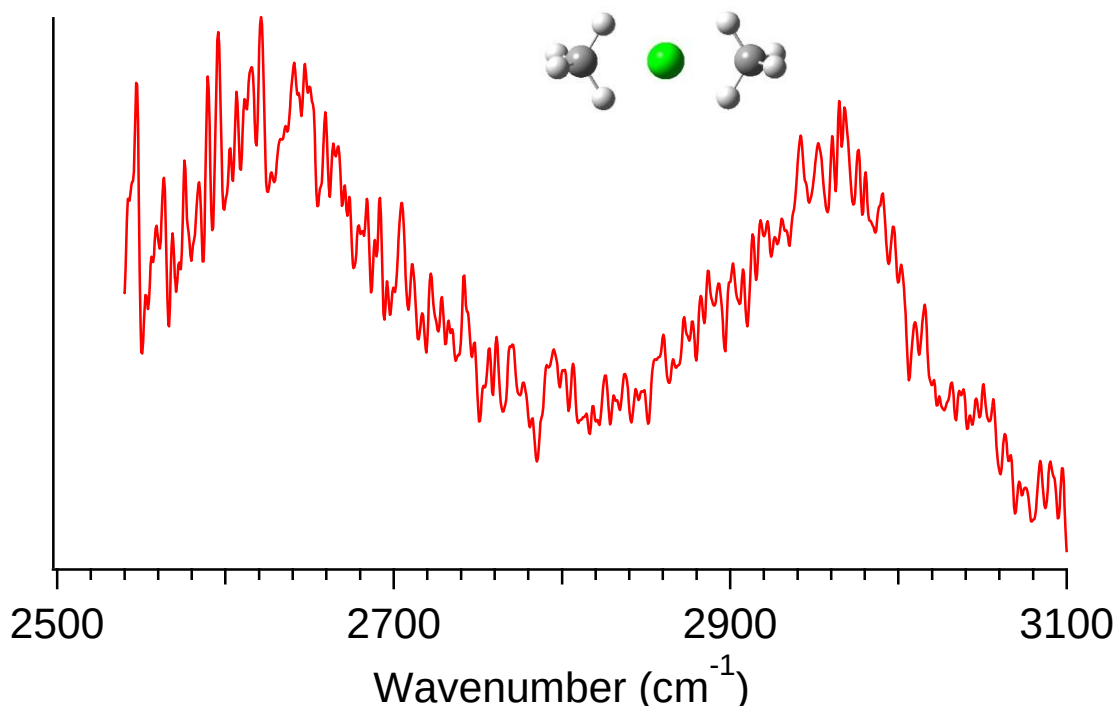


Figure 4.5 IRMPD spectrum of $\text{Ni}^+(\text{CH}_4)_2$ and calculated ground state structure.

The IRMPD spectrum consists of two broad, 100 cm^{-1} fwhm peaks, at 2640 and 2965 cm^{-1} , as shown in Figure 4.5. They are likely due to vibrations of the proximate and distal hydrogens, respectively, but the features are so broad that they are not distinctive.

Vibrational spectra were measured by argon tagging. Figure 4.6 shows the photodissociation spectra of $\text{Co}^+(\text{CH}_4)_2(\text{Ar})$ and $\text{Ni}^+(\text{CH}_4)_2(\text{Ar})$ taken by monitoring Ar loss. The $\text{Co}^+(\text{CH}_4)_2(\text{Ar})$ spectrum shows an intense peak at 2554 cm^{-1} , with weaker features at 2657 and 3049 cm^{-1} . This spectrum is very similar to that of $\text{Co}^+(\text{CH}_4)(\text{Ar})_2$, suggesting that it also has η^2 coordination. Thus, the two low-frequency vibrations are due to the symmetric and antisymmetric C-H stretches of the proximate hydrogens, respectively. The large red shift indicates a strong Co^+ -methane interaction. The weak peak in the high frequency region is due to the antisymmetric distal C-H stretch and it shows little shift from the antisymmetric stretch in

bare CH₄. The corresponding symmetric stretch is too weak to observe. The vibrational spectrum of Ni⁺(CH₄)₂(Ar) is similar to that of the cobalt complex, with the proximate C-H symmetric stretch at 2623 cm⁻¹. This is a smaller red shift than is observed for Co⁺(CH₄)₂(Ar). As with the n=1 clusters, these spectra are qualitatively different from those of M⁺(CH₄)₂ (M=Li,^{16,17} Al,¹⁸ Mn,¹⁹ and Fe²⁰), which have η³ coordination.

There are a few different possible geometries for the n=2 complexes. The methane molecules can have η² or η³ coordination. Previous calculations for Co⁺(CH₄)₂ and Ni⁺(CH₄)₂ predict that the ground state is η², with η³ structures slightly higher in energy.^{22,33,39} All of our calculations converge to η² structures, even when started with an η³ geometry. In addition, the η² complexes can be in two different configurations, with the proximate hydrogens either eclipsed (D_{2h} symmetry, proximate hydrogens square planar) or staggered (D_{2d} symmetry, proximate hydrogens tetrahedral). For cobalt, we calculate a structure with D_{2h} symmetry and a ³B_{2g} ground state, in agreement with the previous studies.^{22,33,39,49} The Co-C bond length is 2.169 Å and the proximate Co-H distances are 1.877 Å. With the geometry restricted to D_{2d}, we obtain a state that lies 1500 cm⁻¹ above the ground state and has imaginary frequencies. This geometry converges to the D_{2h} ground state if the constraints are removed. The orbital occupancy in Co⁺(CH₄)₂ is very similar to that of Co⁺(CH₄). The singly occupied orbitals are **7a_g**([**d_{x²-y²}** + **d_{z²}**]) and **2b_{2g}**(**d_{xz}**). For convenience, Table 4-3 shows the symmetries of d orbitals in different point groups. The calculations predict that Co⁺(CH₄)₂(Ar) forms a Tee-shaped complex with 2.188 Å Co-C bond lengths and a Co-Ar bond length of 2.796 Å with an argon binding energy of 608 cm⁻¹. (Table 4-4) The four heavy atoms and the distal hydrogens are all in the same (yz) plane. The C-Co-C angle is distorted from 180° to 169°. The d orbital electron occupancy is the same as in Co⁺(CH₄)₂, leading to a ³B₁ ground state for this C_{2v} complex (using the same axis system as for Co⁺(CH₄)₂). In Co⁺(CH₄)₂(Ar), the calculated and scaled C-H stretching

frequencies are 2549 and 2672 cm^{-1} for proximate and 2972 and 3056 cm^{-1} for distal hydrogens. The calculations are in good agreement with the experimental values of 2554 and 2657 cm^{-1} (proximate) and 3049 cm^{-1} (antisymmetric distal). Argon tagging is predicted to lead to a small change in the C-H stretches: those from the proximate hydrogens are blue shifted by 17-22 cm^{-1} while the distal C-H stretches are blue shifted by 1 cm^{-1} . Based on the shift between the calculated and experimental frequencies of $\text{Co}^+(\text{CH}_4)_2(\text{Ar})$, the C-H stretches of un-tagged $\text{Co}^+(\text{CH}_4)_2$ are predicted to be 2532 cm^{-1} (symmetric) and 2640 cm^{-1} (antisymmetric) for the proximate hydrogens and 3049 cm^{-1} (antisymmetric distal). As in the case of the $n=1$ complexes, upon binding to Co^+ the symmetric C-H stretches of CH_4 (corresponding to proximate hydrogens in the complex) red shift by 385 and 277 cm^{-1} , confirming that interaction with the metal significantly weakens the C-H bonds in methane.

For $\text{Ni}^+(\text{CH}_4)_2$, Zhang *et al.*²¹ calculate that the ground state and a low-lying excited state have D_{2h} symmetry. We calculate a ^2A_g ground state that is slightly distorted from D_{2h} to C_{2h} by a small shift from η^2 towards η^1 , so that the Ni-H bond lengths are 1.852 Å and 1.863 Å for the proximate hydrogens. The two Ni-C bond lengths are the same: 2.149 Å, and the singly occupied orbital is d_{xz} . In D_{2h} symmetry, this would be a $^2B_{2g}$ state, and it corresponds to the $D_{2h}(x)$ $^2B_{1g}$ state identified as the ground state in the previous calculations.²¹ We also found a ^2A_g state with D_{2h} symmetry 524 cm^{-1} above the ground state. It has 2.198 Å Ni-C bond length and the singly occupied orbital is d_{y^2} . In addition, there is a $^2B_{1g}$ excited state at 1100 cm^{-1} . This corresponds to the $D_{2h}(z)$, $^2B_{1g}$ excited state of Zhang *et al.*²¹ The Ni-C bond length is 2.205 Å, and the singly occupied orbital is d_{xy} . The calculations predict that the lowest frequency C-H stretch in the ground state is distinctive. It is red shifted by >50 cm^{-1} and is >1.5 times more intense than in the excited states. This distinction persists even with argon tagging. Argon binds very weakly to the ground state of $\text{Ni}^+(\text{CH}_4)_2$. The doubly occupied d_{y^2} orbital points directly towards the Ar,

resulting in a very long Ni-Ar bond of 3.345 Å. Instead, the ground state of $\text{Ni}^+(\text{CH}_4)_2(\text{Ar})$ corresponds to the $^2\text{A}_g$ state of $\text{Ni}^+(\text{CH}_4)_2$. The complex is Tee shaped, with a Ni-Ar bond length of 2.569 Å; the Ni-C bonds lengthen slightly to 2.234 Å and the C-Ni-C angle distorts from 180° to 163°. The calculated Ar binding energy (relative to the ground state of $\text{Ni}^+(\text{CH}_4)_2$) is 717 cm^{-1} . Experimentally, the C-H stretches are at 2623, 3001 and 3057 cm^{-1} . The antisymmetric proximate C-H stretch is calculated to be weak and is not experimentally observed. Using the shifts, the C-H stretches in the ground state of un-tagged $\text{Ni}^+(\text{CH}_4)_2$ are predicted to be 2544 cm^{-1} (symmetric) for the proximate and 2959 cm^{-1} (symmetric) and 3067 cm^{-1} (antisymmetric) for the distal hydrogens. These are very similar to the predicted C-H stretching frequencies in $\text{Co}^+(\text{CH}_4)_2$.

Table 4-3 The d orbitals and their symmetries in different point groups in the axis system used in this paper.

	C_s	C_{2v}	D_{2h}
d_{xz}	A''	B_1	B_{2g}
d_{xy}	A'	A_2	B_{1g}
d_{yz}	A''	B_2	B_{3g}
$d_{x^2-y^2}$	A'	A_1	A_g
d_{z^2}	A'	A_1	A_g

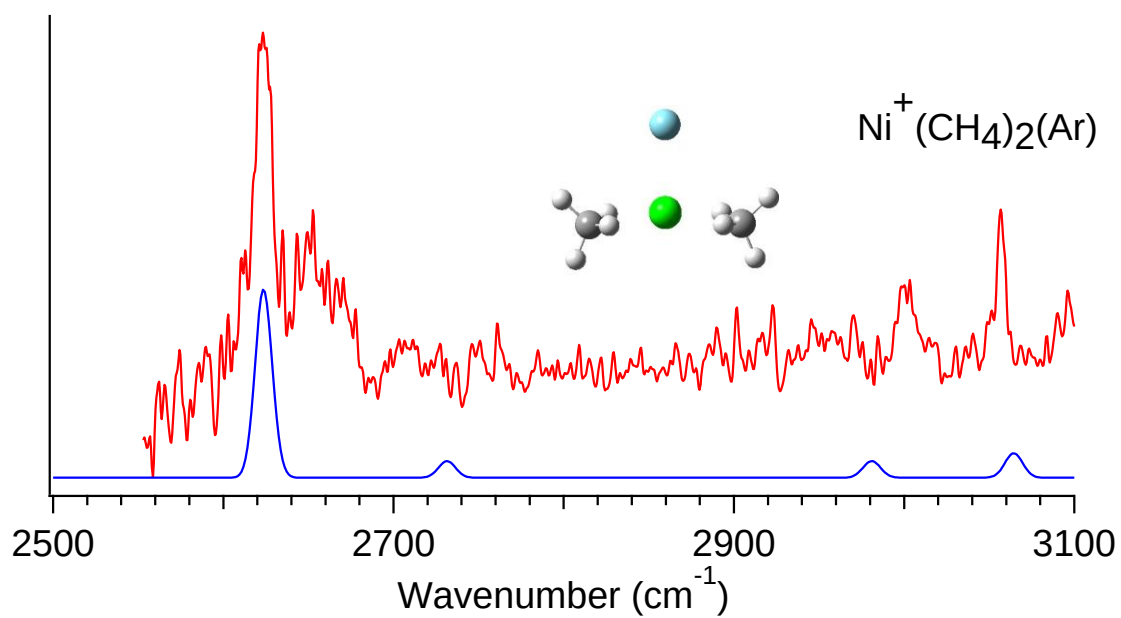
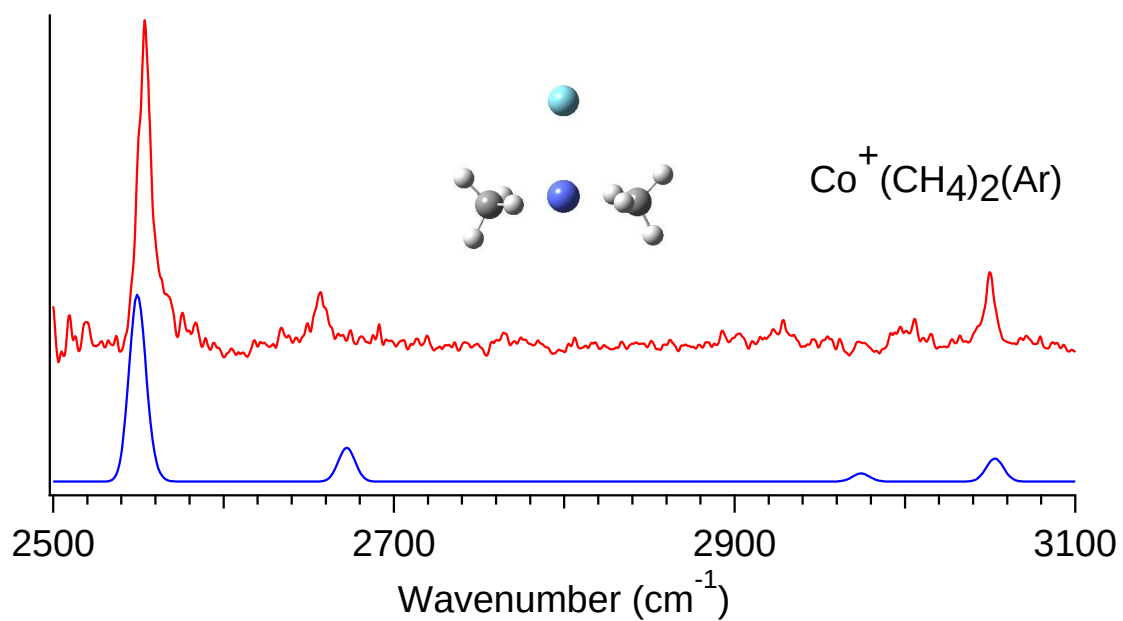


Figure 4.6 Experimental IR photodissociation spectrum of $\text{M}^+(\text{CH}_4)_2(\text{Ar})$ ($\text{M}=\text{Co}, \text{Ni}$) (red), simulated spectra of the calculated ground states (blue), and calculated B3LYP/6-311++G(3df,3pd) structures.

4.3.3 $M^+(CH_4)_3$

The $Co^+(CH_4)_2-CH_4$ and $Ni^+(CH_4)_2-CH_4$ binding energies, measured by guided ion beam³³ and equilibrium^{21,22,35} methods, range from 2550 to 3850 cm^{-1} (Table 4-1) The C-H stretching frequencies are in this region. Therefore, observed one photon dissociation can give useful information on the binding energy. Indeed, efficient dissociation by loss of CH_4 is observed for $Co^+(CH_4)_3$ above 2580 cm^{-1} and for $Ni^+(CH_4)_3$ above 2670 cm^{-1} . Assuming the ions are cold, this provides an upper limit to the bond strength. This is in good agreement with the equilibrium measurement²¹ for $Co^+(CH_4)_2-CH_4$, but it is slightly lower than the other experimental values for $Co^+(CH_4)_2-CH_4$ and $Ni^+(CH_4)_2-CH_4$. The binding energies of the $n=3$ complexes are substantially lower than those of the $n=1$ and 2 complexes. There are two limiting structures for the $n=3$ clusters. The third CH_4 can bind weakly to a nearly unperturbed $M^+(CH_4)_2$ complex, forming a Tee-shaped complex with two short and one long M-C bond. Alternatively, the CH_4 ligands can reorganize to form an equilateral triangular structure, in which all three of the M-C bonds are the same. These two cases can have similar binding energies, but they will lead to very different vibrational spectra.

Figure 4.7 shows vibrational spectra of $Co^+(CH_4)_3$ and $Ni^+(CH_4)_3$ measured by monitoring CH_4 loss. The two spectra are very different. The $Co^+(CH_4)_3$ spectrum consists of multiple peaks between 2580 and 2800 cm^{-1} , the proximate C-H stretch region, and typical distal C-H stretches at 3000 and 3050 cm^{-1} . The vibrational spectrum of $Ni^+(CH_4)_3$ shows a very intense and broad peak at 2694 cm^{-1} with two shoulders at lower frequency, and a very weak distal C-H stretch near 3050 cm^{-1} . The presence of very weak distal C-H stretches and stronger, highly red shifted proximate C-H stretches suggest the complexes have η^2 coordination. The large number of peaks in the proximate C-H stretching region suggest that $Co^+(CH_4)_3$ has several different M-C

bond lengths, and more than one isomer may contribute to the spectrum. The proximate C-H stretches show slightly smaller red shifts in $M^+(CH_4)_3$ than in $M^+(CH_4)_2(Ar)$ and $M^+(CH_4)(Ar)_2$, suggesting that the $n=3$ clusters have longer M-C bonds. Also, $Ni^+(CH_4)_3$ shows a smaller red shift than $Co^+(CH_4)_3$. The spectrum of the nickel complex is qualitatively similar to that of $Fe^+(CH_4)_3$, which has η^2 coordination.²⁰

Previous calculations on $Co^+(CH_4)_3$ identified two nearly degenerate states: a Tee-shaped structure with C_{2v} symmetry in which the third CH_4 binds weakly to the ground state of $Co^+(CH_4)_2$, resulting in two short Co-C bonds and a long Co-C bond, and an equilateral triangular structure with D_3 symmetry in which all three Co-C bonds are equal.^{22,33} Our calculations confirm these results. All of the other possible geometries are either higher in energy or relax to these two structures. The ground state is predicted to be the Tee-shaped structure with two short Co-C bonds (2.225 Å), a C-Co-C angle of 162° and one long Co-C bond (2.580 Å). All three of the ligands have η^2 coordination, and the proximate hydrogens are perpendicular to the plane containing the heavy atoms. The equilateral triangular structure is calculated to lie only 24 cm^{-1} above the ground state. The Co-C bond lengths are all 2.298 Å and the proximate hydrogens are in η^2 coordination and are twisted, at a 31° angle to the plane of the heavy atoms.

Figure 4.7 shows calculated, scaled vibrational spectra of the Tee-shaped (solid line) and equilateral (dashed line) structures of $Co^+(CH_4)_3$. For the Tee-shaped ground state, the most red-shifted peak shown (2583 cm^{-1}) is due to the symmetric stretch of the proximate hydrogens belonging to the short Co-C bonds; the corresponding antisymmetric stretch is the small peak at 2699 cm^{-1} . The peak at 2743 cm^{-1} is due to the symmetric C-H stretch belonging to the CH_4 that is further from the metal, the corresponding antisymmetric stretch is at 2890 cm^{-1} . In the equilateral structure, all three Co-C bonds are equal and intermediate; this leads to much simpler spectrum, with the proximate C-H stretches at 2635 cm^{-1} (symmetric) and 2734 cm^{-1}

(antisymmetric). In each case, a shorter Co-C bond leads to a larger red shift in the proximate C-H stretch. Clearly neither spectrum alone matches the experiment. However, a combination of the two in a 4:1 (Tee:equilateral) ratio provides a good match to the observed spectrum as shown in the lower trace. The presence of the two isomers is not surprising considering the calculations predict that they are nearly degenerate. In fact, changing the source conditions results in slightly different relative ratios of the peaks at 2586 and 2627 cm^{-1} . The spectrum shown was taken under the coldest conditions, which favors the peaks due to the Tee-shaped structure, suggesting that this is the actual ground state. In addition, the Tee-shaped structure of $\text{Co}^+(\text{CH}_4)_3$ is similar to that of $\text{Co}^+(\text{CH}_4)_2(\text{Ar})$, with two methane molecules close to the metal and the third ligand far away. The vibrational spectra of the C-H stretches of the nearby methanes are also very similar, at 2586 and 2682 cm^{-1} in $\text{Co}^+(\text{CH}_4)_3$ and 2554 and 2657 cm^{-1} in $\text{Co}^+(\text{CH}_4)_2(\text{Ar})$. The slightly larger red shift for the Ar-tagged complex implies a smaller Co-C bond length.

As with $\text{Co}^+(\text{CH}_4)_3$, previous calculations on $\text{Ni}^+(\text{CH}_4)_3$ identified two nearly degenerate states: a nearly equilateral structure and a Tee-shaped structure.²¹ We find the ground state to be the nearly equilateral structure with C_{2v} symmetry with two long (2.323 Å) and one short (2.234 Å) Ni-C bonds. All three of the methane ligands have η^2 coordination and the proximate hydrogens of the long Ni-C bonds are perpendicular to the plane containing the heavy atoms while the proximate hydrogens of the third CH_4 are in the plane of the heavy atoms. The Tee-shaped structure is calculated to lie only 117 cm^{-1} above the ground state. It has one long (2.364 Å) and two short (2.279 Å) Ni-C bonds with a C-Ni-C angle of 150°. The proximate hydrogens are in η^2 coordination and all of them are perpendicular to the plane of the heavy atoms.

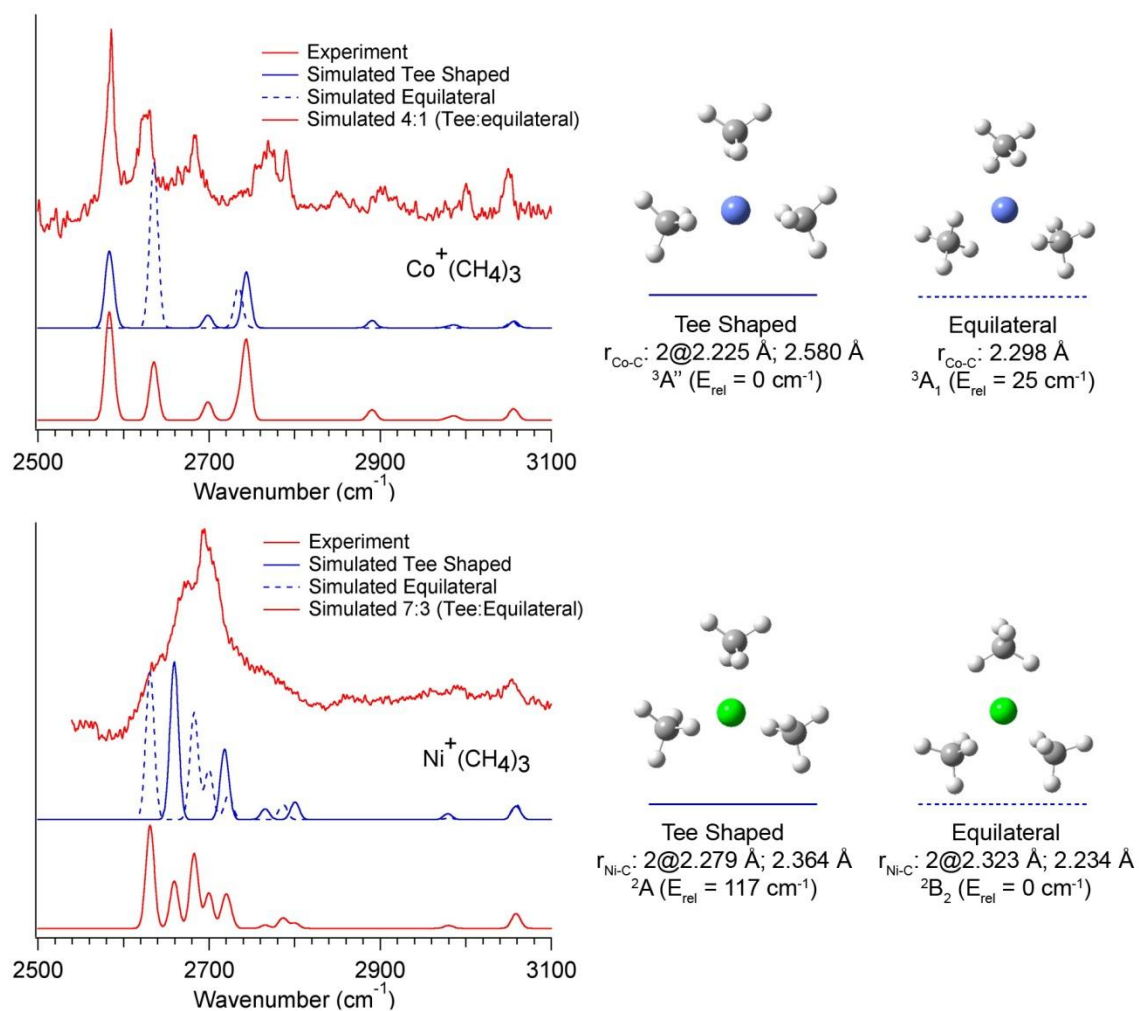


Figure 4.7 Experimental IR photodissociation spectra of $\text{M}^+(\text{CH}_4)_3$ ($\text{M}=\text{Co}, \text{Ni}$) (upper red trace), simulated spectra of low lying states (blue), best mixture of low lying states (lower red trace) and corresponding calculated B3LYP/6-311++G(3df,3pd) structures. The solid lines are from Tee-shaped structures and dashed lines are from equilateral structures.

While the truly equilateral triangular structure of the cobalt complex leads to a very simple spectrum, the distorted triangular structure of the nickel complex gives rise to a rather complex spectrum. Figure 4.7 shows calculated, scaled vibrational spectra for the Tee-shaped (solid line) and equilateral (dashed line) structures of $\text{Ni}^+(\text{CH}_4)_3$. For the equilateral ground state, the most red-shifted peak (2631 cm^{-1}) is due to the symmetric stretch of the proximate hydrogens belonging to the nearby CH_4 . The next two peaks are due to the same mode of the distant CH_4 ligands, in phase (2682 cm^{-1}) and out of phase (2700 cm^{-1}). The corresponding antisymmetric stretches are at 2723 cm^{-1} (nearby CH_4) and 2786 cm^{-1} (in phase mode of distant methanes; the out of phase mode is not IR active). In the Tee-shaped structure of $\text{Ni}^+(\text{CH}_4)_3$, the most red shifted peak (2659 cm^{-1}) is due to the symmetric stretch of the proximate hydrogens of the two nearby methanes; the analogous vibration of the more distant methane is at 2718 cm^{-1} . The corresponding antisymmetric stretches are the weak peaks at 2766 and 2800 cm^{-1} . The Tee-shaped nickel complex significantly differs from the analogous cobalt complex. In $\text{Co}^+(\text{CH}_4)_3$, the third methane is far from the metal and barely perturbs the $\text{Co}^+(\text{CH}_4)_2$ core, whereas in nickel the three Ni-C bond lengths are quite similar. As a result, the calculated vibrational spectra of the Tee-shaped structures of the nickel and cobalt complexes are quite different.

The experimental spectrum of $\text{Ni}^+(\text{CH}_4)_3$ consists mainly of a broad peak, from 2600 to 2820 cm^{-1} , and the lowest lying vibrations are shoulders of the peak at 2692 cm^{-1} . No single simulation provides a good match to the experimental spectrum. However, the combination of the Tee-shaped and semi equilateral spectra in a 7:3 (Tee:equilateral) ratio (shown in the bottom trace in Figure 4.7) matches the observed spectrum above 2670 cm^{-1} . However, the lowest-lying absorption of the equilateral triangular structure is the most intense, which is at odds with the rapidly decreasing intensity in the photodissociation spectrum below 2670 cm^{-1} . This discrepancy may be due to the energy of this vibration being below the binding energy of

the third CH₄, so absorption may not always lead to dissociation. If that is the case, then the observed dissociation onset is not merely an upper limit, but is the actual dissociation energy. This gives a value of 2650±50 cm⁻¹ for the binding energy of Ni⁺(CH₄)₂-CH₄. This is between the equilibrium measurement²¹ of 3250 cm⁻¹ and the calculated B3LYP value of 2495 cm⁻¹, and somewhat below the CAM-B3LYP value of 2948 cm⁻¹.

The vibrational spectra of M⁺(CH₄)₃ (M = Mn, Fe, Co, Ni) have been measured and the structures of the clusters can be compared. The manganese cluster has a Mn⁺ (⁷S, 3d⁵4s¹) core. This leads to a pyramidal cluster with η³ methane ligands, which is clearly different from that of later metals which have a 3dⁿ4s⁰ M⁺ core. This asymmetric arrangement maximizes polarization of the 4s electron on the metal.¹⁹ The other metals show η² coordination and the heavy atoms are co-planar, leading to a competition between nearly degenerate Tee-shaped and (quasi) equilateral triangular structures.

4.3.4 M⁺(CH₄)₄

The measured methane binding energies of the n=4 complexes are significantly smaller than those of the smaller clusters: 1820 cm⁻¹ for Co⁺(CH₄)₄ and 1920 cm⁻¹ for Ni⁺(CH₄)₄ (Table 4-1).^{21,22,35} Our calculated binding energies are somewhat lower: 735 and 1147 cm⁻¹, respectively. Our calculated binding energies are somewhat lower: 735 and 1030 cm⁻¹, respectively. Observation of high dissociation yields for the n=4 complexes is consistent with these low binding energies.

Figure 4.8 shows vibrational spectra of Co⁺(CH₄)₄ and Ni⁺(CH₄)₄ measured by monitoring CH₄ loss. The Co⁺(CH₄)₄ spectrum consists of three intense peaks at 2631 cm⁻¹, 2801 cm⁻¹ (with a shoulder at 2785 cm⁻¹), and at 2845 cm⁻¹, along with a broad, weak peak near 2900 cm⁻¹, and the typical distal C-H stretch at 2993 cm⁻¹. The vibrational spectrum of Ni⁺(CH₄)₄ is extremely simple.

The spectrum is dominated by an intense feature at 2749 cm^{-1} . There are weak peaks at 2696 , 2831 and 2867 cm^{-1} . The distal C-H stretches are very weak, at 2943 and 2996 cm^{-1} . The simplicity of the nickel spectrum suggests that it is highly symmetrical. For $\text{Co}^+(\text{CH}_4)_4$, the large number of peaks in the proximate C-H stretching region suggest that the ligands are at several different distances from the metal, and more than one isomer may contribute to the spectrum as in the case of the $n=3$ complexes. Both complexes do not show any intense peaks in the distal C-H stretch region, suggesting lack of η^3 coordination.

For $\text{Co}^+(\text{CH}_4)_4$, our calculations predict two nearly degenerate geometries. One is a distorted square planar structure with C_{2h} symmetry and Co-C bond lengths of 2.277 and $2.709\text{ \AA}$. The proximate hydrogens of the nearest ligands have η^2 coordination with a Co-H distance of $1.950\text{ \AA}$ while the hydrogens of the more distant ligands are distorted towards η^1 coordination with Co-H distances of 2.132 and $2.470\text{ \AA}$. This structure corresponds to the ground state identified by Zhang *et al.*²² The distorted square planar structure with equal Co-C bond lengths but unequal C-Co-C angles, proposed by Haynes *et al.*³³ was found to relax to the C_{2h} structure. The second structure, calculated to lie 188 cm^{-1} below the first, has a quasi-tetrahedral geometry with C_{2v} symmetry. It has Co-C bond lengths of $2.411\text{ \AA}$ (with proximate Co-H distances of 1.922 and $2.189\text{ \AA}$) and $2.514\text{ \AA}$ (with proximate Co-H distances of 1.998 and $2.284\text{ \AA}$). Another quasi-tetrahedral structure with three unequal Co-C bonds, proposed by Zhang *et al.*²² was found to relax to the C_{2v} structure.

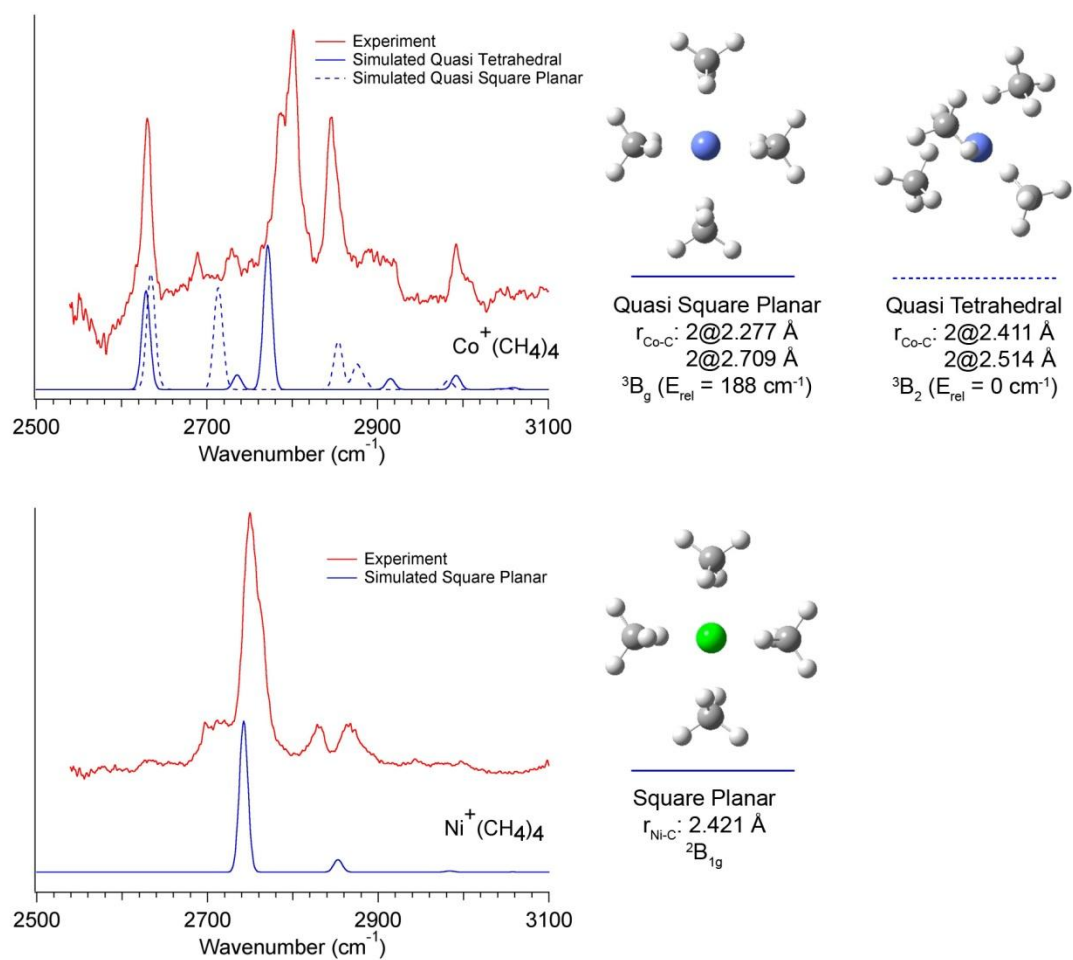


Figure 4.8 Experimental IR photodissociation spectra of $\text{M}^+(\text{CH}_4)_4$ ($\text{M}=\text{Co}, \text{Ni}$) (red), simulated spectra of the calculated low lying states (blue) and corresponding calculated B3LYP/6-311++G(3df,3pd) structures..

Figure 4.8 shows the experimental IR photodissociation spectrum of $\text{Co}^+(\text{CH}_4)_4$ along with simulated spectra. The simulation belonging to the C_{2h} (planar) structure (solid line) reproduces many of the features in the experimental spectrum. The peak calculated at 2629 cm^{-1} is due to the symmetric stretch of the proximate hydrogens belonging to nearby methane ligands; the corresponding antisymmetric stretch is the weaker peak at 2735 cm^{-1} . Also the symmetric and antisymmetric C-H stretches of the distant methanes, calculated to be 2771 and 2914 cm^{-1} , generally match the observed peaks. However, the simulated spectrum of the C_{2h} structure does not predict the peak at 2845 cm^{-1} , suggesting an additional isomer is present. Although the simulation of the C_{2v} (quasi-tetrahedral) structure (dashed line) reproduces this peak as well as the feature at 2631 cm^{-1} , it also predicts an intense peak near 2715 cm^{-1} , which is not observed. The poor match of the C_{2v} isomer suggests that another structure may be responsible for the peak at 2845 cm^{-1} . However, optimizations run from many different starting geometries all converged to the C_{2h} or C_{2v} structures.

The situation for $\text{Ni}^+(\text{CH}_4)_4$ is much more straightforward (Figure 4.8). Our calculations predict that the ground state is a square planar structure with D_{4h} symmetry and $2.421\text{ \AA}$ Ni-C bond length. All of the proximate hydrogens are in η^2 coordination and perpendicular to the plane of the heavy atoms. This corresponds to the ground state calculated by Zhang *et al.*,²¹ which has the hole in the $d_{x^2-y^2}$ orbital. Here we use the coordinate system of Zhang *et al.*, which has the ligands on the x and y axes, so this orbital points directly towards the four ligands. We also considered the quasi-tetrahedral structure they find to lie somewhat higher in energy. However, at our level of theory, this structure converges to the square planar structure. Since the square planar structure is highly symmetrical, the calculated spectrum is very simple. It is dominated by the peak at 2742 cm^{-1} , which is due to the symmetric stretch of the proximate hydrogens; the corresponding antisymmetric stretch gives rise to the small peak at 2854 cm^{-1} .

The distal C-H stretches are calculated to be extremely weak (<1 km/mol). The simulated spectrum of the square planar structure provides an excellent match to the experiment. The calculated (and observed) structures of $M^+(CH_4)_4$ ($M = Mn, Fe, Co, Ni$) reflect a competition between two limiting cases: square planar and tetrahedral. $Mn^+(CH_4)_4$ adopts a slightly distorted tetrahedral geometry with the methane ligands in η^3 coordination.¹⁹ All the other metals have η^2 coordinate $n=4$ complexes. $Ni^+(CH_4)_4$ adopts a highly symmetrical square planar structure. The geometry of the iron complex is similar to that of the nickel complex: symmetrical square planar and tetrahedral structures are calculated to be essentially degenerate and the observed spectrum does not favor either structure. In contrast, the calculations predict highly distorted square planar and quasi-tetrahedral structures for $Co^+(CH_4)_4$. Thus the observed spectrum is very complex.

4.4 Summary and Conclusions

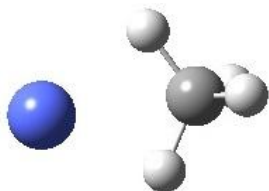
In this work, we present vibrational spectra of $M^+(CH_4)_n(Ar)_m$ ($n=1-4$; $m=0-2$; $M=Co, Ni$) obtained by monitoring loss of either CH_4 or Ar following IR photo-excitation. Calculations predict that the positions and intensities of bands in the C-H stretching region depend strongly on the coordination of the CH_4 to the metal (η^1 , η^2 or η^3) and on the M-C bond length. Thus, we determine the structures of the complexes by comparing the observed IR photodissociation spectra to calculated vibrational spectra of low-lying candidate structures. The vibrational spectra show that all of the complexes adopt configurations with η^2 methane coordination (sometimes distorted towards η^1), in accord with theoretical predictions. The binding energies of the $n=1$ and 2 clusters is so high that they require three photons to dissociate, therefore no photodissociation is observed. The spectra of the argon tagged complexes are measured. Even with argon tagging, the $n=1$ and 2 complexes show very large red shifts in the proximate C-H

stretching frequencies of up to 370 cm^{-1} relative to bare CH_4 . The large red shift reflects a covalent contribution to the M^+-CH_4 binding, concomitant with weakening of the proximate C-H bonds. The larger clusters have much smaller binding energies. Consequently, spectra are measured using single IR photon dissociation. The spectra of the $n=3$ complexes reveal a competition between nearly degenerate Tee-shaped and equilateral structures. The observed, spectroscopic, onset of the $\text{Co}^+(\text{CH}_4)_3$ spectrum provides an upper limit: $D_0(\text{Co}^+(\text{CH}_4)_2-\text{CH}_4) < 2580\text{ cm}^{-1}$, while the onset observed for $\text{Ni}^+(\text{CH}_4)_3$ appears to be thermodynamic, giving $D_0(\text{Ni}^+(\text{CH}_4)_2-\text{CH}_4) = 2650 \pm 50\text{ cm}^{-1}$. $\text{Ni}^+(\text{CH}_4)_4$ has a highly symmetrical square planar structure, with the unpaired electron in the $d_{x^2-y^2}$ orbital. In contrast, $\text{Co}^+(\text{CH}_4)_4$ has two nearly degenerate, highly distorted structures.

Table 4-4 Calculated electronic states and structures for $M^+(\text{CH}_4)_n(\text{Ar})_m$, $M=\text{Co, Ni}$; $n=1-4$; $m=0-2$

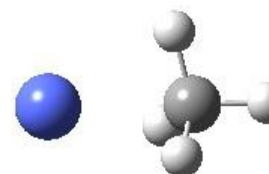
$\text{Co}^+(\text{CH}_4)$

Sym	State	E(no ZPE, Hartree)	E(w/ZPE,Hartree)	Atom	X	Y	Z
C_{2v}	$^3\text{B}_1$	-1422.99410668	-1422.94934100	Co	0.000000	0.000000	0.586432
				C	0.000000	0.000000	-1.572679
				H	0.000000	0.899712	-2.181726
				H	0.975584	0.000000	-1.017069
				H	-0.975584	0.000000	-1.017069
				H	0.000000	-0.899712	-2.181726



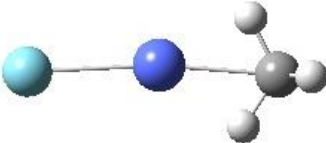
Frequency (Intensity): 58.5 (0.1), 313.8 (1.2), 493.6 (1.5), 1158.6 (25.9), 1379.1 (3.3), 1438.8 (35.1), 1469.7 (0.0), 1581.8 (0.7), 2693.5 (44.8), 2787.3 (8.6), 3102.6 (6.6), 3172.7 (14.3).

Sym	State	E(no ZPE, Hartree)	E(w/ZPE,Hartree)	Atom	X	Y	Z
C_{3v}	$^3\text{A}_1$	-1422.99178866	-1422.94825400	Co	0.000000	0.000000	0.570250
				C	0.000000	0.000000	-1.513392
				H	0.000000	1.072243	-1.237575
				H	0.928589	-0.536121	-1.237575
				H	-0.928589	-0.536121	-1.237575
				H	0.000000	0.000000	-2.603664



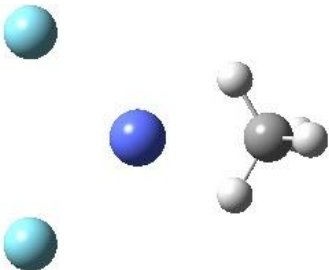
Frequency (Intensity): -212.8 (0.0), -211.0 (0.0), 328.1 (3.0), 1241.3 (35.1), 1334.9 (18.2), 1335.0 (18.3), 1510.2 (9.1), 1510.3 (9.0), 2843.6 (24.0), 2952.3 (0.4), 2952.3 (0.4), 3101.6 (40.1).

Co⁺(CH₄)Ar

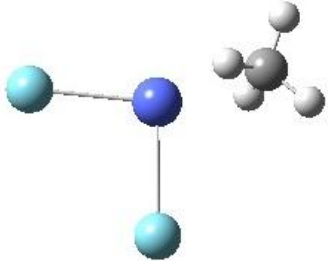
Sym	State	E(no ZPE, Hartree)	E(w/ZPE,Hartree)	Atom	X	Y	Z
C _{2v}	³ B ₁	-1950.56609565	-1950.52040800	Co	0.385682	0.069037	-0.000005
				C	2.530325	-0.098533	0.000011
				H	3.139486	-0.138552	0.898421
				H	1.906691	-1.029638	-0.000131
				H	2.040814	0.912253	-0.000001
				H	3.139655	-0.138443	-0.898291
				Ar	-1.990112	-0.0488	0.000003

Frequency (Intensity): 28.9 (0.0), 33.4 (0.1), 101.1 (0.4), 182.7 (6.3), 332.0 (2.3), 543.3 (1.2), 1162.4 (19.5), 1385.2 (4.3), 1444.5 (36.6), 1468.1 (0.0), 1594.7 (1.4), 2696.8 (37.4), 2801.3 (6.3), 3106.1 (4.3), 3174.0 (10.6).

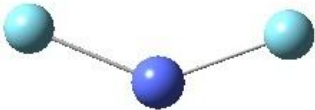
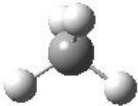
Co⁺(CH₄)(Ar)₂

Sym	State	E(no ZPE, Hartree)	E(w/ZPE,Hartree)	Atom	X	Y	Z
C _{2v}	³ B ₁	-2478.12613286	-2478.07962800	Co	0.000000	0.000000	0.587533
				C	0.000000	0.000000	2.783846
				H	0.896954	0.000000	3.396280
				H	0.000000	0.966494	2.222698
				H	0.000000	-0.966494	2.222698
				H	-0.896954	0.000000	3.396280
				Ar	0.000000	-1.766065	-1.216789
				Ar	0.000000	1.766065	-1.216789

Frequency (Intensity): 41.7 (0.1), 61.0 (0.2), 62.4 (0.9), 88.3 (0.0), 114.1 (8.2), 135.6 (0.5), 147.8 (6.7), 293.7 (1.9), 540.0 (9.6), 1177.7 (18.0), 1380.1 (3.8), 1440.7 (47.8), 1481.9 (0.0), 1592.6 (1.2), 2743.9 (41.0), 2832.6 (18.0), 3106.5 (2.0), 3172.7 (6.6).

Sym	State	E(no ZPE, Hartree)	E(w/ZPE,Hartree)	Atom	X	Y	Z
C ₁	³ A	-2478.12568064	-2478.07901200		-0.167308	0.572869	0.151778
					-2.049155	1.640720	-0.190479
					-2.121741	2.718654	-0.082348
					-1.375293	1.439023	-1.056950
					-1.788270	1.230690	0.818789
					-3.009875	1.203361	-0.446894
					2.229803	0.175704	-0.090494
					-0.834946	-1.948122	-0.031046

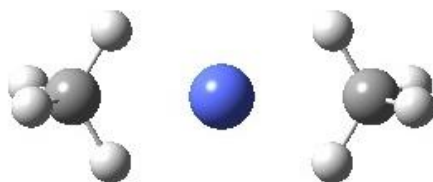
Frequency (Intensity): 46.0 (0.3), 48.9 (0.8), 59.7 (0.1), 107.2 (7.8), 135.6 (0.2), 158.8 (5.8), 183.6 (0.8), 298.8 (1.9), 525.7 (2.4), 1177.8 (20.8), 1383.0 (5.2), 1438.3 (37.6), 1480.3 (0.3), 1595.2 (1.2), 2730.7 (40.2), 2833.5 (9.2), 3107.7 (2.0), 3174.3 (6.3).

C _{2v}	³ B ₁	-2478.12353758	-2478.07717500	Co	0.000000	0.000000	0.141095
				C	0.000000	0.000000	2.368274
				H	0.000000	0.896406	2.981154
				H	-0.960589	0.000000	1.800646
				H	0.960589	0.000000	1.800646
				H	0.000000	-0.896406	2.981154
				Ar	0.000000	2.341821	-0.766189
				Ar	0.000000	-2.341821	-0.766189

Frequency (Intensity): 26.9 (0.1), 28.4 (1.5), 59.3 (0.2), 120.8 (2.6), 145.0 (1.5), 149.1 (13.0), 150.8 (0.0), 276.9 (1.6), 434.5 (1.6), 1183.7 (24.3), 1382.4 (4.0), 1427.7 (32.9), 1480.1 (0.0), 1593.3 (0.1), 2762.4 (51.9), 2846.9 (7.9), 3108.4 (0.7), 3174.2 (5.3).

Co⁺(CH₄)₂

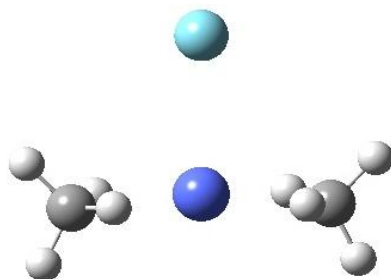
Sym	State	E(no ZPE, Hartree)	E(w/ZPE, Hartree)	Atom	X	Y	Z
D _{2h}	³ B _{2g}	-1463.568101	-1463.476148	Co	0.000000	0.000000	0.000000
				C	2.168587	0.000000	0.000000
				H	2.779997	0.000000	0.897568
				H	1.607530	0.968609	0.000000
				H	2.779997	0.000000	-0.897568
				H	1.607530	-0.968609	0.000000
				C	-2.168587	0.000000	0.000000
				H	-2.779997	0.000000	-0.897568
				H	-1.607530	-0.968609	0.000000
				H	-1.607530	0.968609	0.000000
				H	-2.779997	0.000000	0.897568



Frequency (Intensity): 47.4 (0.1), 83.0 (0.0), 103.6 (1.1), 171.8 (0.0), 205.2 (3.5), 302.6 (0.0), 347.0 (1.8), 566.7 (0.0), 669.3 (9.2), 1170.5 (0.0), 1173.3 (34.2), 1388.2 (0.0), 1388.7 (10.1), 1449.6 (0.0), 1463.6 (101.4), 1474.7 (0.0), 1478.5 (0.0), 1603.2 (3.2), 1606.9 (0.0), 2719.9 (76.3), 2728.5 (0.0), 2821.5 (0.0), 2832.8 (12.3), 3108.3 (0.0), 3108.3 (6.2), 3174.8 (0.0), 3175.1 (16.1).

Co⁺(CH₄)₂Ar

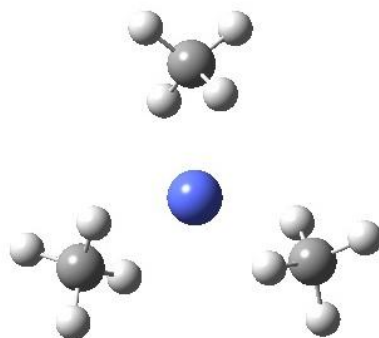
Sym	State	E(no ZPE, Hartree)	E(w/ZPE, Hartree)	Atom	X	Y	Z
C _{2v}	³ B ₁	-1991.125543	-1991.032801	27	0.000000	0.000000	0.713149
				18	0.000000	2.178856	0.914052
				6	0.000000	2.922739	0.122550
				6	0.964221	1.623864	0.810047
				1	0.000000	2.645137	1.894405
				1	-0.964221	1.623864	0.810047
				1	0.000000	-2.178856	0.914052
				1	0.000000	-2.645137	1.894405
				1	-0.964221	-1.623864	0.810047
				1	0.964221	-1.623864	0.810047
				1	0.000000	-2.922739	0.122550
				1	0.000000	0.000000	-2.083207



Frequency (Intensity): 56.1 (1.1), 69.6 (2.7), 74.9 (4.5), 96.2 (0.8), 134.9 (0.0), 143.6 (0.2), 186.1 (0.0), 212.9 (2.1), 290.1 (0.2), 330.6 (1.6), 537.6 (0.0), 647.0 (8.8), 1179.4 (1.3), 1182.9 (36.0), 1386.9 (0.1), 1387.1 (12.2), 1440.5 (0.0), 1452.5 (83.5), 1484.2 (12.5), 1484.9 (0.0), 1600.9 (2.0), 1605.2 (0.1), 2739.7 (74.3), 2746.8 (3.8), 2837.5 (0.0), 2848.0 (13.2), 3109.2 (0.0), 3109.2 (3.4), 3175.2 (0.4), 3175.4 (10.1).

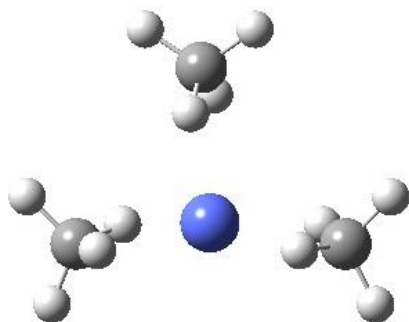
Co⁺(CH₄)₃

Sym	State	E(no ZPE, Hartree)	E(w/ZPE, Hartree)	Atom	X	Y	Z
D ₃	³ A ₁	-1504.11399977	-1503.975684	Co	0.000000	0.000000	0.000000
				C	0.000000	2.297608	0.000000
				C	1.989787	-1.148804	0.000000
				C	-1.989787	-1.148804	0.000000
				H	0.490419	1.722768	0.813641
				H	-0.490419	1.722768	-0.813641
				H	0.765172	2.911873	-0.464993
				H	-0.765172	2.911873	0.464993
				H	-1.246752	-1.286099	-0.813641
				H	-1.737170	-0.436669	0.813641
				H	-2.904342	-0.793278	-0.464993
				H	-2.139170	-2.118595	0.464993
				H	1.246752	-1.286099	0.813641
				H	1.737170	-0.436669	-0.813641
				H	2.904342	-0.793278	0.464993
				H	2.139170	-2.118595	-0.464993



Frequency (Intensity): 55.4 (0.0), 55.5 (0.0), 83.6 (0.4), 127.8 (0.0), 127.8 (0.0), 148.0 (0.0), 197.2 (0.0), 199.8 (0.0), 199.9 (0.0), 237.9 (4.9), 238.0 (4.9), 253.2 (0.0), 495.1 (12.4), 506.0 (3.8), 506.0 (3.8), 1198.5 (10.1), 1205.4 (20.1), 1205.4 (20.1), 1373.3 (0.0), 1375.5 (7.6), 1375.5 (7.6), 1428.0 (14.7), 1428.0 (14.7), 1428.1 (92.1), 1493.8 (0.1), 1493.8 (0.1), 1497.2 (0.0), 1585.7 (0.7), 1585.7 (0.7), 1593.4 (0.0), 2816.5 (90.2), 2816.5 (90.1), 2825.5 (0.0), 2901.6 (26.4), 2902.1 (9.3), 2902.1 (9.3), 3110.0 (0.0), 3110.2 (0.0), 3110.2 (0.0), 3173.6 (2.0), 3173.6 (2.4), 3173.6 (2.4).

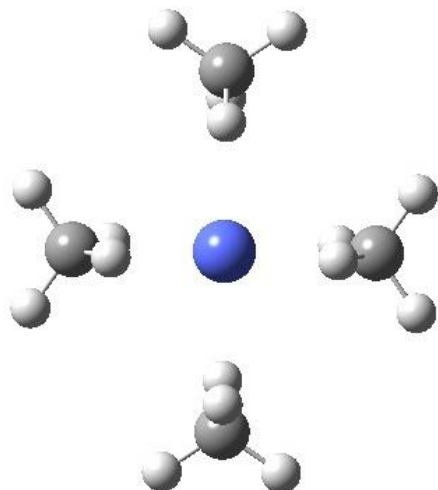
Sym	State	E(no ZPE, Hartree)	E(w/ZPE, Hartree)	Atom	X	Y	Z
C _{2v}				C	0.000002	-2.252060	-0.003273
				H	-0.893925	-2.862634	0.084271
				H	-0.000002	-1.549661	0.848530
				H	0.893939	-2.862620	0.084266
				C	2.196736	0.684133	-0.003217
				H	2.971174	-0.074789	0.055249
				H	1.653339	0.508785	-0.959813
				H	2.624945	1.680229	-0.059613
				H	1.628548	0.627879	0.954396
				C	-2.196737	0.684131	-0.003217
				H	-1.653337	0.508790	-0.959813
				H	-1.628548	0.627884	0.954396
				H	-2.971168	-0.074799	0.055249
				H	-2.624955	1.680223	-0.059613
				Co	0.000000	0.328411	0.001770
				H	-0.000005	-1.773601	-0.987060



Frequency (Intensity): 61.9 (0.1), 65.3 (0.2), 80.7 (0.3), 108.4 (0.9), 111.2 (0.0), 135.4 (0.1), 152.6 (2.9), 182.7 (0.0), 205.7 (1.8), 216.1 (0.0), 238.9 (2.8), 271.5 (0.0), 302.5 (2.4), 489.2 (0.0), 605.4 (8.8), 1186.5 (1.0), 1190.5 (33.9), 1253.7 (17.0), 1348.0 (13.0), 1381.7 (3.5), 1381.8 (11.9), 1384.7 (22.5), 1431.2 (0.0), 1445.7 (93.3), 1485.5 (0.1), 1488.0 (0.0), 1534.4 (0.1), 1563.9 (2.9), 1592.8 (1.7), 1599.2 (0.1), 2770.2 (79.0), 2775.5 (9.5), 2863.2 (0.2), 2871.5 (14.0), 2910.1 (60.9), 3036.4 (8.1), 3110.5 (0.0), 3110.6 (1.3), 3117.9 (3.0), 3169.2 (0.0), 3175.7 (0.3), 3175.8 (7.0).

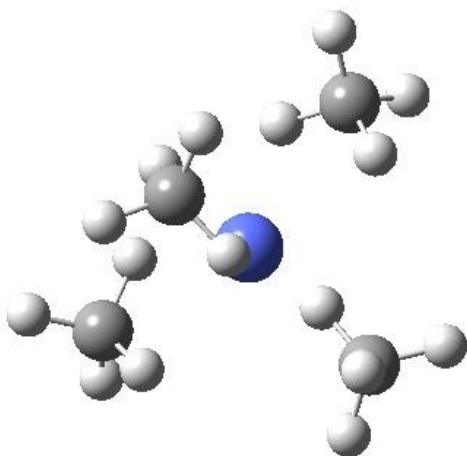
Co⁺(CH₄)₄

Sym	State	E(no ZPE, Hartree)	E(w/ZPE, Hartree)	Atom	X	Y	Z
C _{2h}		-1544.65569956	-1544.471125	Co	0.000000	0.000000	0.000000
				C	0.000000	-2.277239	-0.000002
				H	0.078460	-1.702968	0.947398
				H	-0.078459	-1.702964	-0.947400
				H	-0.893002	-2.889888	0.074239
				H	0.893002	-2.889888	-0.074245
				C	-0.000001	2.277239	-0.000002
				H	-0.078462	1.702965	-0.947401
				H	0.078461	1.702967	0.947398
				H	-0.893003	2.889888	0.074242
				H	0.893000	2.889889	-0.074246
				C	-2.708564	-0.000001	-0.002981
				H	-2.259735	-0.000010	-0.998095
				H	-1.970180	0.000003	0.814471
				H	-3.318023	0.892411	0.107788
				H	-3.318028	-0.892407	0.107802
				C	2.708564	0.000000	0.002984
				H	1.970181	0.000003	-0.814468
				H	2.259734	-0.000009	0.998098
				H	3.318023	0.892412	-0.107785
				H	3.318028	-0.892407	-0.107797



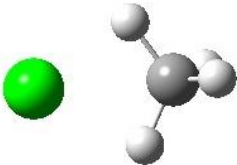
Frequency (Intensity): 24.8 (0.1), 73.4 (0.4), 80.7 (2.0), 88.9 (0.0), 93.9 (0.0), 97.4 (2.0), 105.4 (0.0), 109.1 (0.0), 123.5 (5.3), 163.9 (0.0), 177.4 (0.0), 201.4 (2.5), 208.0 (0.1), 223.4 (0.0), 232.9 (0.0), 249.7 (0.0), 250.8 (0.0), 266.9 (3.2), 278.2 (3.1), 428.8 (0.0), 578.8 (5.6), 1204.1 (0.0), 1209.4 (42.3), 1272.5 (0.0), 1272.6 (28.8), 1344.1 (0.0), 1344.7 (24.8), 1376.6 (0.0), 1377.4 (49.2), 1381.0 (13.0), 1382.1 (0.0), 1419.2 (0.0), 1437.3 (79.4), 1495.9 (0.0), 1497.3 (0.1), 1541.0 (0.0), 1542.6 (0.3), 1558.2 (4.0), 1558.5 (0.0), 1592.5 (0.1), 1599.3 (0.0), 2810.5 (88.7), 2812.3 (0.0), 2896.1 (0.0), 2903.1 (13.1), 2931.2 (0.0), 2934.3 (129.6), 3054.0 (0.0), 3057.4 (9.9), 3113.6 (0.0), 3113.6 (0.0), 3121.7 (0.0), 3121.9 (12.8), 3164.6 (0.0), 3164.7 (0.7), 3178.0 (0.0), 3178.1 (1.6).

Sym	State	E(no ZPE, Hartree)	E(w/ZPE, Hartree)	Atom	X	Y	Z
C _{2v}		-1544.65601314	-1544.471983	Co	0.000000	-0.000001	0.004704
				C	2.392955	-0.000012	-0.771932
				H	3.001418	-0.894327	-0.869152
				H	3.001427	0.894300	-0.869129
				H	1.981875	-0.000024	0.255256
				H	1.648979	0.000002	-1.575271
				C	-0.000013	-2.289493	0.755453
				H	0.894972	-2.838758	1.031793
				H	-0.894999	-2.838770	1.031771
				H	-0.000029	-1.358609	1.364229
				H	-0.000002	-2.162614	-0.334125
				C	-2.392955	0.000015	-0.771932
				H	-3.001416	0.894332	-0.869150
				H	-3.001429	-0.894295	-0.869130
				H	-1.648980	0.000001	-1.575272
				H	-1.981875	0.000024	0.255257
				C	0.000014	2.289493	0.755454
				H	-0.894971	2.838759	1.031794
				H	0.895000	2.838768	1.031774
				H	0.000004	2.162615	-0.334124
				H	0.000027	1.358607	1.364228

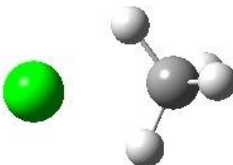


Frequency (Intensity): 24.4 (0.2), 48.0 (2.3), 62.7 (0.0), 78.0 (0.1), 87.1 (0.0), 107.2 (0.0), 117.8 (0.7), 139.3 (2.4), 144.0 (0.0), 144.6 (0.0), 161.1 (0.0), 161.7 (9.3), 168.9 (7.3), 217.7 (1.1), 218.4 (0.4), 230.2 (3.6), 234.2 (0.0), 303.6 (0.3), 314.0 (0.7), 394.3 (0.9), 447.4 (1.8), 1217.8 (0.0), 1224.2 (31.2), 1246.7 (0.0), 1247.0 (36.6), 1347.4 (16.4), 1348.1 (12.4), 1357.7 (13.5), 1358.9 (2.9), 1392.9 (13.5), 1395.5 (30.0), 1409.1 (1.3), 1416.0 (65.2), 1512.8 (0.0), 1513.1 (0.3), 1530.2 (0.0), 1530.6 (1.5), 1568.7 (6.8), 1569.1 (1.0), 1581.7 (3.2), 1592.2 (0.2), 2814.7 (104.0), 2824.5 (3.3), 2882.7 (67.2), 2885.7 (29.2), 3003.9 (24.5), 3006.2 (20.5), 3023.2 (21.3), 3031.2 (8.0), 3114.1 (0.9), 3114.3 (2.7), 3115.0 (4.4), 3115.9 (0.1), 3169.8 (0.0), 3169.8 (0.1), 3172.5 (0.6), 3172.5 (0.0).

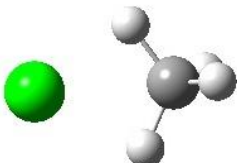
Ni⁺(CH₄)

Sym	State	E(no SCF, Hartree)	E(w/ZPE, Hartree)	Atom	X	Y	Z
C _s	² A'	-1548.536385	-1548.491421	Ni	0.000324	-0.576407	0.000000
				C	0.005366	1.604974	0.000000
				H	-0.936147	0.987307	0.000000
				H	-0.052021	2.206815	0.902340
				H	-0.052021	2.206815	-0.902340
				H	0.998927	1.108609	0.000000

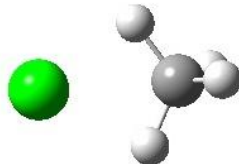
Frequency (Intensity): 91.8 (0.3), 277.0 (5.3), 503.6 (2.3), 1161.8 (28.1), 1362.5 (6.5), 1429.9 (34.0), 1479.5 (0.5), 1581.9 (4.7), 2692.6 (68.1), 2871.6 (23.1), 3105.9 (7.5), 3179.0 (15.4).

Sym	State	E(no SCF, Hartree)	E(w/ZPE, Hartree)	Atom	X	Y	Z
C _{2v}	² A ₁	-1548.535789	-1548.489835	Ni	0.000000	0.000000	0.586214
				C	0.000000	0.000000	-1.63306
				H	0.000000	0.962494	-1.07222
				H	0.000000	-0.962494	-1.07222
				H	-0.903513	0.000000	-2.23559
				H	0.903513	0.000000	-2.23559

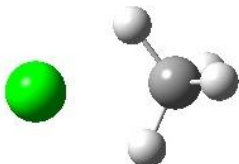
Frequency (Intensity): 137.0 (0.4), 298.4 (1.8), 745.6 (0.7), 1172.8 (29.0), 1360.6 (12.0), 1408.6 (40.8), 1496.2 (0.0), 1567.7 (12.7), 2776.2 (42.2), 2922.0 (6.1), 3105.9 (9.0), 3180.4 (14.0).

Sym	State	E(no SCF, Hartree)	E(w/ZPE, Hartree)	Atom	X	Y	Z
C _{2v}	² B ₁	-1548.535461	-1548.490746	Ni	0.000000	0.000000	0.567576
				C	0.000000	0.000000	-1.580032
				H	0.000000	0.972814	-1.021118
				H	0.000000	-0.972814	-1.021118
				H	-0.902199	0.000000	-2.184848
				H	0.902199	0.000000	-2.184848

Frequency (Intensity): -28.0 (0.4), 322.3 (2.1), 515.6 (0.8), 1150.4 (28.6), 1373.8 (2.1), 1443.1 (0.0), 1443.5 (33.8), 1573.9 (0.2), 2713.8 (70.5), 2806.7 (5.5), 3105.5 (7.4), 3179.2 (17.3).

Sym	State	E(no SCF, Hartree)	E(w/ZPE, Hartree)	Atom	X	Y	Z
C _s	² A'	-1548.535462	-1548.490691	Ni	0.000893	-0.567385	0.000000
							
		C	0.000893	1.579308	0.000000		
		H	-0.047780	1.021840	0.972390		
		H	-0.047780	1.021840	-0.972390		
		H	-0.868124	2.231790	0.000000		
		H	0.933337	2.135459	0.000000		

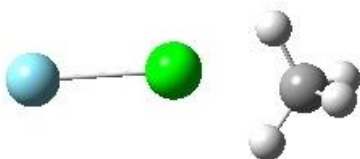
Frequency (Intensity): 27.4 (0.4), 322.9 (2.1), 512.5 (0.8), 1151.4 (28.7), 1372.9 (2.2), 1433.8 (17.4), 1452.8 (16.4), 1572.7 (0.4), 2714.3 (70.0), 2807.1 (5.4), 3104.9 (7.8), 3179.1 (17.2).

Sym	State	E(no SCF, Hartree)	E(w/ZPE, Hartree)	Atom	X	Y	Z
C _{2v}	² A ₂	-1548.532953	-1548.488174	Ni	0.000000	0.000000	0.580596
							
		C	0.000000	0.000000	-1.615695		
		H	0.000000	0.969399	-1.061894		
		H	0.000000	-0.969399	-1.061894		
		H	-0.902995	0.000000	-2.219369		
		H	0.902995	0.000000	-2.219369		

Frequency (Intensity): 132.6 (0.2), 320.7 (2.2), 349.0 (5.3), 1160.6 (26.1), 1355.0 (9.4), 1396.7 (36.4), 1493.0 (0.0), 1560.8 (13.1), 2764.2 (53.7), 2842.7 (14.5), 3102.9 (9.4), 3178.0 (15.8).

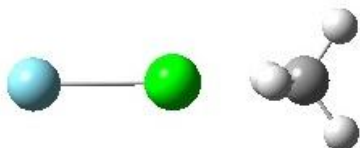
Ni⁺(CH₄)Ar

Sym	State	E(no SCF, Hartree)	E(w/ZPE, Hartree)	Atom	X	Y	Z
C _s	² A'	-2076.109909	-2076.063925	Ni	0.000000	0.376233	0.000000
				C	0.866968	2.381652	0.000000
				H	1.046865	2.961231	0.900404
				H	1.585573	1.537725	0.000000
				H	-0.238173	2.172934	0.000000
				H	1.046865	2.961231	-0.900404
				Ar	-0.480163	-1.914308	0.000000



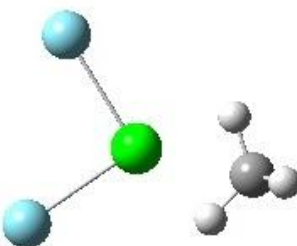
Frequency (Intensity): 51.1 (0.1), 62.9 (0.0), 138.6 (0.8), 188.1 (4.6), 286.8 (8.5), 514.6 (2.2), 1170.2 (22.9), 1366.7 (9.0), 1431.7 (35.1), 1482.0 (0.7), 1598.6 (7.1), 2706.3 (50.6), 2896.2 (19.7), 3110.5 (4.5), 3180.5 (10.2).

C _{2v}	² A ₁	-2076.109373	-2076.061796	Ni	0.000000	0.000000	0.354338
				C	0.000000	0.000000	2.575974
				H	0.000000	0.901607	3.180730
				H	-0.958608	0.000000	2.011166
				H	0.958608	0.000000	2.011166
				H	0.000000	-0.901607	3.180730
				Ar	0.000000	0.000000	-1.986728

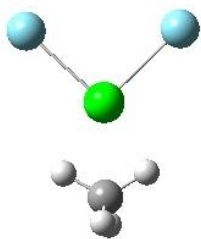


Frequency (Intensity): 59.7 (0.1), 98.9 (0.0), 181.0 (1.0), 188.6 (5.4), 306.2 (5.3), 968.1 (100.8), 1182.8 (24.4), 1367.0 (14.9), 1413.1 (63.0), 1497.0 (0.0), 1581.4 (16.3), 2789.3 (39.7), 2958.5 (88.6), 3110.1 (5.9), 3182.0 (9.2).

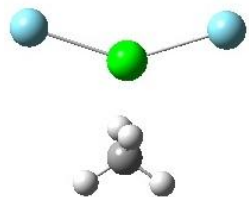
Ni⁺(CH₄)(Ar)₂

Sym	State	E (no ZPE, Hartree)	E (w/ZPE, Hartree)	Atom	X	Y	Z
C _s	² A'	-2603.671904	-2603.62523	Ni	0.527326	-0.069110	0.000070
				C	2.659803	-0.557046	-0.000114
				H	3.252396	-0.695948	-0.899192
				H	2.328206	0.508121	-0.000339
				H	1.892113	-1.367370	0.000052
				H	3.252469	-0.695586	0.898971
				Ar	-1.488772	-1.456832	0.000764
				Ar	-0.756803	2.008993	-0.000212

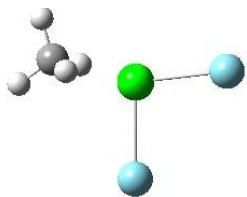
Frequency (Intensity): 34.3 (0.1), 63.1 (0.0), 70.4 (0.7), 101.9 (0.4), 117.7 (0.3), 140.5 (8.6), 163.1 (6.1), 298.7 (3.8), 535.9 (6.2), 1173.7 (18.2), 1373.6 (3.0), 1438.3 (31.4), 1474.5 (0.0), 1582.6 (0.4), 2772.8 (69.6), 2855.7 (18.3), 3111.0 (2.0), 3180.2 (8.3).

Sym	State	E(no ZPE, Hartree)	E(w/ZPE, Hartree)	Atom	X	Y	Z
C _{2v}	² B ₁	-2603.671854	-2603.625376	Ni	0.000000	0.000000	0.516328
				C	0.000000	0.000000	2.705388
				H	0.899058	0.000000	3.314091
				H	0.000000	0.962547	2.141112
				H	0.000000	-0.962547	2.141112
				H	-0.899058	0.000000	3.314091
				Ar	0.000000	-1.781205	-1.155553
				Ar	0.000000	1.781205	-1.155553

Frequency (Intensity): -12.4 (0.2), 59.2 (0.0), 65.0 (0.8), 98.4 (0.0), 104.7 (0.6), 139.1 (8.6), 161.5 (6.1), 294.8 (3.7), 518.4 (7.0), 1173.9 (18.1), 1373.1 (2.9), 1436.1 (32.4), 1474.3 (0.0), 1582.0 (0.4), 2774.6 (70.0), 2856.5 (18.2), 3110.3 (2.0), 3179.4 (8.2).

Sym	State	E(no ZPE, Hartree)	E(w/ZPE, Hartree)	Atom	X	Y	Z
C _{2v}	² A ₁	-2603.670389	-2603.623505	Ni	0.000000	0.000000	0.055421
				C	0.000000	0.000000	2.313494
				H	0.000000	0.898821	2.922084
				H	-0.952019	0.000000	1.740990
				H	0.952019	0.000000	1.740990
				H	0.000000	-0.898821	2.922084
				Ar	0.000000	2.318099	-0.687747
				Ar	0.000000	-2.318099	-0.687747

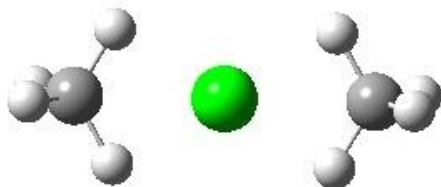
Frequency (Intensity): 49.1 (1.3), 56.8 (0.0), 64.0 (0.2), 135.4 (2.0), 146.3 (0.0), 177.4 (14.5), 214.1 (0.8), 290.1 (1.8), 367.8 (3.1), 1205.7 (23.8), 1368.3 (13.1), 1404.9 (37.1), 1511.0 (0.0), 1586.1 (7.7), 2818.8 (39.7), 2891.9 (9.8), 3111.9 (1.7), 3180.5 (4.1).

Sym	State	E(no SCF, Hartree)	E(w/ZPE, Hartree)	Atom	X	Y	Z
C _s	² A'	-2603.671695	-2603.624974	Ni	0.000000	0.534835	0.000000
				C	1.546802	2.135422	0.000000
				H	1.230671	3.173614	0.000000
				H	1.207498	1.678481	0.955954
				H	1.207498	1.678481	-0.955954
				H	2.629067	2.043485	0.000000
				Ar	-2.186203	-0.443333	0.000000
				Ar	1.322006	-1.576776	0.000000

Frequency (Intensity): 57.1 (0.4), 58.7 (0.6), 65.4 (0.0), 112.7 (0.0), 137.7 (7.9), 166.5 (5.3), 206.3 (1.3), 307.4 (3.2), 374.3 (2.0), 1199.0 (22.1), 1366.9 (16.8), 1404.6 (41.1), 1507.7 (1.2), 1584.6 (13.1), 2800.3 (36.5), 2882.9 (4.2), 3109.8 (4.1), 3179.2 (5.6).

Ni⁺(CH₄)₂

Sym	State	E(no ZPE, Hartree)	E(w/ZPE, Hartree)		X	Y	Z
C _{2h}	² A _g	-1589.110948	-1589.019395	Ni	0.000000	0.000000	0.000000
				C	0.000000	2.149074	0.000000
				H	-0.009012	2.756473	0.899822
				H	-0.965319	1.580923	0.000000
				H	-0.009012	2.756473	-0.899822
				H	0.968373	1.591731	0.000000
				C	0.000000	-2.149074	0.000000
				H	0.009012	-2.756473	-0.899822
				H	0.965319	-1.580923	0.000000
				H	-0.968373	-1.591731	0.000000
				H	0.009012	-2.756473	0.899822



Frequency (Intensity): 41.1 (0.0), 71.6 (0.0), 96.6 (1.3), 110.9 (0.5), 173.8 (3.5), 290.7 (0.0), 360.5 (3.7), 534.2 (0.0), 642.0 (7.4), 1164.9 (0.0), 1169.2 (37.4), 1380.9 (0.0), 1381.2 (9.9), 1441.3 (0.0), 1457.7 (90.6), 1460.1 (0.0), 1476.3 (0.2), 1593.8 (2.5), 1596.7 (0.0), 2736.4 (119.3), 2742.8 (0.0), 2832.4 (0.0), 2846.4 (9.8), 3111.5 (0.0), 3111.5 (7.3), 3181.3 (0.0), 3181.3 (20.3).

Sym	State	E(no ZPE, Hartree)	E(w/ZPE, Hartree)		X	Y	Z
D _{2h}	² B _{2g}	-1589.110818	-1589.019257	Ni	0.000000	0.000000	0.000000
				C	2.141988	0.000000	0.000000
				H	2.749556	0.000000	0.899774
				H	1.579402	0.967675	0.000000
				H	2.749556	0.000000	-0.899774
				H	1.579402	-0.967675	0.000000
				C	-2.141988	0.000000	0.000000
				H	-2.749556	0.000000	-0.899774
				H	-1.579402	-0.967675	0.000000
				H	-1.579402	0.967675	0.000000
				H	-2.749556	0.000000	0.899774



Frequency (Intensity): -13.0 (0.0), 34.4 (0.0), 95.8 (1.3), 130.9 (0.0), 146.5 (4.2), 304.8 (0.0), 362.1 (3.6), 563.9 (0.0), 672.3 (7.5), 1161.2 (0.0), 1165.8 (36.8), 1383.6 (0.0), 1384.0 (7.0), 1449.2 (0.0), 1466.7 (92.9), 1467.9 (0.0), 1471.8 (0.0), 1595.2 (0.7), 1598.5 (0.0), 2732.2 (129.0), 2740.9 (0.0), 2837.4 (0.0), 2840.0 (8.7), 3111.5 (0.0), 3111.6 (6.8), 3181.2 (21.0), 3181.2 (0.0).

Sym	State	E(no ZPE, Hartree)	E(w/ZPE, Hartree)		X	Y	Z
D _{2h}	² B _{1g}	-1589.105319	-1589.014471	Ni	0.000000	0.000000	0.000000
				C	2.204759	0.000000	0.000000
				H	2.811218	0.000000	0.900498
				H	1.645077	0.962464	0.000000
				H	2.811218	0.000000	-0.900498
				H	1.645077	-0.962464	0.000000
				C	-2.204759	0.000000	0.000000
				H	-2.811218	0.000000	-0.900498
				H	-1.645077	-0.962464	0.000000
				H	-1.645077	0.962464	0.000000
				H	-2.811218	0.000000	0.900498



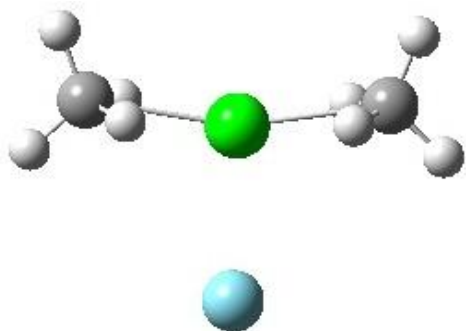
Frequency (Intensity): 50.4 (0.0), 65.5 (0.1), 73.1 (1.6), 141.2 (0.0), 180.7 (1.4), 299.1 (0.0), 319.6 (0.0), 349.4 (4.4), 412.3 (3.8), 1177.2 (0.0), 1179.8 (37.3), 1362.9 (28.8), 1364.0 (0.0), 1395.4 (0.0), 1413.0 (81.8), 1502.1 (0.0), 1503.4 (0.0), 1572.9 (32.5), 1585.3 (0.0), 2790.3 (95.4), 2798.6 (0.0), 2870.2 (0.0), 2890.0 (8.9), 3109.7 (0.0), 3109.8 (9.6), 3180.8 (18.7), 3180.9 (0.0).

Sym	State	E(no ZPE, Hartree)	E(w/ZPE, Hartree)		X	Y	Z
D _{2h}	² A _g	-1589.108475	-1589.017008	Ni	0.000000	0.000000	0.000000
				C	2.197926	0.000000	0.000000
				H	2.804742	0.000000	0.900196
				H	1.634417	0.961677	0.000000
				H	2.804742	0.000000	-0.900196
				H	1.634417	-0.961677	0.000000
				C	-2.197926	0.000000	0.000000
				H	-2.804742	0.000000	-0.900196
				H	-1.634417	-0.961677	0.000000
				H	-1.634417	0.961677	0.000000
				H	-2.804742	0.000000	0.900196

Frequency (Intensity): 71.1 (0.1), 78.9 (1.6), 103.2 (0.0), 153.9 (0.0), 241.7 (2.4), 297.0 (0.0), 350.8 (3.7), 384.0 (0.0), 391.5 (3.2), 1187.5 (0.0), 1191.8 (42.1), 1367.1 (33.6), 1368.0 (0.0), 1406.5 (86.6), 1485.2 (0.0), 1491.5 (0.0), 1506.4 (0.0), 1579.1 (35.3), 1590.8 (0.0), 2777.8 (69.0), 2784.2 (0.0), 2876.3 (5.7), 2882.6 (0.0), 3110.4 (0.0), 3110.5 (11.3), 3180.8 (0.0), 3181.1 (16.1).

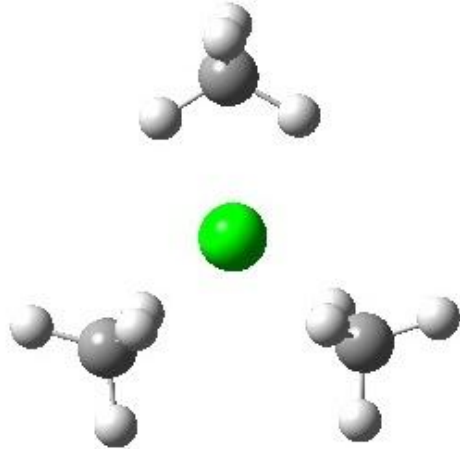
Ni⁺(CH₄)₂Ar

Sym	State	E(no ZPE, Hartree)	E(w/ZPE, Hartree)		X	Y	Z
C _{2v}	² B ₁	-2116.66876549	-2116.576667	Ni	0.000000	0.000000	0.598859
				C	0.000000	2.207882	0.936251
				H	0.000000	3.000810	0.194378
				H	0.954281	1.655839	0.792850
				H	0.000000	2.602593	1.947156
				H	-0.954281	1.655839	0.792850
				C	0.000000	-2.207882	0.936251
				H	0.000000	-2.602593	1.947156
				H	-0.954281	-1.655839	0.792850
				H	0.954281	-1.655839	0.792850
				H	0.000000	-3.000810	0.194378
				Ar	0.000000	0.000000	-1.969862



Frequency (Intensity): 65.6 (1.1), 73.8 (0.2), 74.7 (1.3), 108.1 (0.0), 116.2 (7.6), 126.7 (0.0), 199.2 (0.5), 242.5 (0.9), 282.3 (0.2), 324.4 (3.3), 335.1 (0.0), 363.8 (2.6), 1202.9 (4.0), 1206.4 (38.6), 1365.4 (36.4), 1367.2 (0.9), 1400.4 (81.0), 1400.7 (0.0), 1510.0 (0.8), 1511.2 (0.0), 1578.2 (26.5), 1590.0 (0.3), 2807.6 (67.1), 2811.0 (3.1), 2879.4 (0.0), 2900.4 (6.0), 3111.4 (0.0), 3111.5 (6.1), 3180.1 (0.8), 3180.2 (8.2).

$\text{Ni}^+(\text{CH}_4)_3$

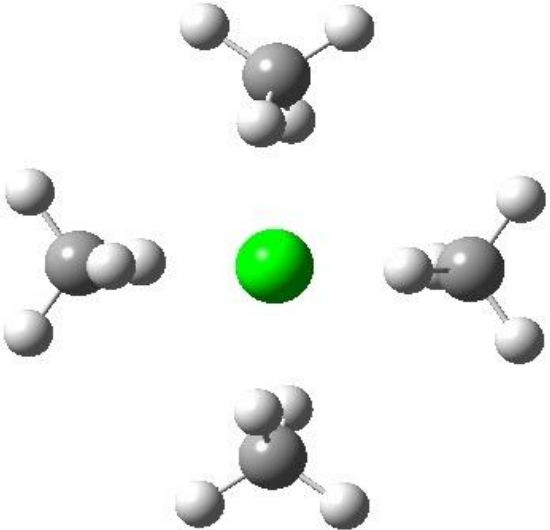
Sym	State	E(no ZPE, Hartree)	E(w/ZPE, Hartree)	Atom	X	Y	Z
C_{2v}	$^2B_2$	-1629.661308	-1629.5236	Ni	0.000000	0.000000	0.132395
				C	0.000000	1.773884	-1.368121
				H	0.000000	1.687869	-2.450364
				H	-0.942305	1.319929	-1.007455
				H	0.942305	1.319929	-1.007455
				H	0.000000	2.812138	-1.051636
				C	0.000000	-1.773884	-1.368121
				H	0.942305	-1.319929	-1.007455
				H	-0.942305	-1.319929	-1.007455
				H	0.000000	-1.687869	-2.450364
				H	0.000000	-2.812138	-1.051636
				C	0.000000	0.000000	2.366191
				H	0.000000	0.955078	1.796734
				H	0.000000	-0.955078	1.796734
				H	0.897663	0.000000	2.976797
				H	-0.897663	0.000000	2.976797

Frequency (Intensity): 38.9 (0.1), 63.2 (0.0), 63.3 (0.0), 81.4 (0.1), 118.3 (2.8), 130.1 (0.0), 181.2 (0.1), 186.2 (0.0), 229.8 (3.1), 263.4 (0.2), 268.4 (0.0), 284.2 (6.1), 304.1 (0.0), 309.0 (1.1), 512.4 (6.8), 1186.9 (15.4), 1215.5 (14.3), 1228.8 (24.2), 1361.5 (19.4), 1368.0 (7.4), 1371.7 (8.6), 1394.3 (0.0), 1398.3 (72.0), 1433.0 (35.7), 1484.1 (0.0), 1513.7 (0.0), 1523.1 (0.0), 1572.1 (9.1), 1580.7 (3.3), 1592.4 (2.6), 2812.3 (77.0), 2857.4 (56.1), 2872.4 (26.4), 2892.4 (12.9), 2934.1 (0.0), 2947.3 (8.0), 3111.6 (0.5), 3113.0 (0.2), 3113.4 (0.2), 3178.0 (1.3), 3178.4 (1.7), 3178.5 (5.1).

Sym	State	E(no ZPE, Hartree)	E(w/ZPE, Hartree)	Atom	X	Y	Z
C ₂	² A	-1629.660593	-1629.523068	C	0.000000	2.201165	0.797361
				C	0.000000	-2.201165	0.797361
				C	0.000000	0.000000	-2.159510
				H	-0.136031	2.461924	1.842048
				H	-0.920690	1.680203	0.459634
				H	0.960364	1.659801	0.697887
				H	0.086096	3.086324	0.173956
				H	0.933854	0.092068	-1.577268
				H	-0.933854	-0.092068	-1.577268
				H	-0.087358	0.892878	-2.770729
				H	0.087358	-0.892878	-2.770729
				H	-0.960364	-1.659801	0.697887
				H	0.920690	-1.680203	0.459634
				H	0.136031	-2.461924	1.842048
				H	-0.086096	-3.086324	0.173956
				Ni	0.000000	0.000000	0.204917

Frequency (Intensity): 54.7 (0.1), 65.7 (0.9), 76.0 (0.6), 82.7 (0.0), 121.4 (0.6), 159.0 (0.0), 173.5 (0.4), 207.9 (0.4), 242.7 (3.7), 244.4 (0.3), 249.5 (0.8), 269.3 (0.0), 292.9 (4.1), 323.5 (0.1), 343.1 (1.7), 1210.0 (1.7), 1215.7 (31.1), 1230.4 (26.2), 1359.3 (15.5), 1360.7 (34.3), 1365.7 (1.1), 1391.6 (10.6), 1398.2 (97.5), 1398.5 (0.5), 1515.3 (0.0), 1515.5 (1.1), 1524.7 (0.0), 1570.3 (6.1), 1574.9 (21.5), 1592.4 (0.2), 2836.3 (16.0), 2836.9 (67.0), 2887.7 (36.8), 2916.9 (0.1), 2929.3 (5.6), 2959.2 (9.2), 3111.4 (0.0), 3111.5 (3.1), 3114.0 (0.0), 3177.8 (0.3), 3178.0 (4.6), 3178.1 (2.2).

Ni⁺(CH₄)₄

Sym	State	E(no ZPE, Hartree)	E(w/ZPE, Hartree)	Atom	X	Y	Z
D _{4h}	² B _{1g}	-1670.205834	-1670.021129	Ni	0.000000	0.000000	0.000000
				C	0.000000	2.421026	0.000000
				H	0.000000	1.834430	0.932799
				H	0.000000	1.834430	-0.932799
				H	-0.896107	3.033671	0.000000
				H	0.896107	3.033671	0.000000
				C	0.000000	-2.421026	0.000000
				H	0.000000	-1.834430	0.932799
				H	0.000000	-1.834430	-0.932799
				H	-0.896107	-3.033671	0.000000
				H	0.896107	-3.033671	0.000000
				C	2.421026	0.000000	0.000000
				H	1.834430	0.000000	0.932799
				H	1.834430	0.000000	-0.932799
				H	3.033671	0.896107	0.000000
				H	3.033671	-0.896107	0.000000
				C	-2.421026	0.000000	0.000000
				H	-1.834430	0.000000	0.932799
				H	-1.834430	0.000000	-0.932799
				H	-3.033671	0.896107	0.000000
				H	-3.033671	-0.896107	0.000000

Frequency (Intensity): 16.0 (0.0), 82.5 (1.8), 106.9 (0.4), 106.9 (0.4), 116.7 (0.0), 124.5 (0.0), 145.4 (0.0), 165.7 (0.0), 165.7 (0.0), 193.2 (0.0), 214.2 (5.3), 214.2 (5.3), 216.5 (0.0), 226.8 (0.0), 241.9 (0.0), 246.1 (0.0), 246.1 (0.0), 274.3 (2.3), 274.3 (2.3), 279.9 (1.1), 292.7 (0.0), 1228.9 (0.0), 1245.7 (39.8), 1245.7 (39.8), 1256.5 (0.0), 1351.0 (0.0), 1358.6 (31.6), 1358.6 (31.6), 1367.8 (0.0), 1383.2 (0.0), 1387.5 (0.0), 1387.5 (0.0), 1391.4 (128.2), 1518.8 (0.0), 1532.7 (0.0), 1532.7 (0.0), 1545.7 (0.0), 1559.9 (0.0), 1570.4 (7.9), 1570.4 (7.9), 1593.8 (0.0), 2896.6 (0.0), 2909.5 (90.2), 2909.5 (90.2), 2921.7 (0.0), 2974.0 (0.0), 2977.8 (0.0), 2977.8 (0.0), 3004.2 (14.9), 3114.0 (0.0), 3115.2 (0.7), 3115.2 (0.7), 3116.5 (0.0), 3175.8 (0.0), 3176.8 (0.1), 3176.8 (0.1), 3177.6 (0.0).

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- [49] We use the same coordinate system as for the n=1 complexes, with the M-C bond on the z axis, and proximate hydrogens in the xz plane. Our (x,y,z) is equivalent to (y,z,x) used by Bowers and coworkers. Thus, their d_{xy} orbital (B_{1g}) becomes d_{xz} (B_{2g}). Similarly, our (x,y,z) corresponds to (y,x,z) used by Armentrout, Goddard and coworkers. So their B_{3g} corresponds to our B_{2g} . All of their states have been converted to our axis system.

CHAPTER 5

VIBRATIONAL SPECTROSCOPY OF $\text{Cu}^+(\text{CH}_4)_n$ AND $\text{Ag}^+(\text{CH}_4)_n$ ($n=1-6$)

5.1 Introduction

As discussed in the previous chapter, metals with a $3d^n 4s^0$ ground state (such as Co^+ and Ni^+) interact more strongly with ligands than those with $3d^{n-1} 4s^1$ (such as Mn^+). An extension to these metal ions with empty 4s orbitals is Cu^+ and Ag^+ , which have a d^{10} ground state. These ions lie between open shell transition metal ions such as quartet Fe^+ , Co^+ and Ni^+ , all of which have the 4s orbital empty and 3d partially filled, and transition metal ions such as Zn^+ and Mn^+ , which have filled or half filled 3d orbitals and a 4s electron. Thus one can expect that the Cu^+-CH_4 binding energy will be high, similar to those of Co^+ and Ni^+ , but symmetrical $\text{Cu}^+(\text{CH}_4)_n$ complexes will be preferred as the directional d orbitals are equally occupied, as is the case with Mn^+ and Zn^+ . In addition, comparing Cu^+ and Ag^+ complexes provides an opportunity to understand how the metal-methane interaction depends on the size of the metal. The ionic radii of Cu(I) and Ag(I) are 0.77 Å and 1.15 Å, respectively.¹ Besides their interesting orbital occupancies Cu^+ and Ag^+ are in their regular oxidation states. So, fundamental interactions of these metals with CH_4 ligands in the gas phase are more directly related to their character in the condensed phase systems.

Previous spectroscopic studies of $\text{M}^+(\text{CH}_4)_n$ complexes include the electronic spectra of $\text{Mg}^+(\text{CH}_4)$,² $\text{Ca}^+(\text{CH}_4)$,³ $\text{V}^+(\text{CH}_4)$,⁴ and $\text{Zn}^+(\text{CH}_4)$,⁵ and vibrational spectroscopy of $\text{Li}^+(\text{CH}_4)_{1-6}$,^{6,7} $\text{Al}^+(\text{CH}_4)_{1-6}$,⁸ $\text{Mn}^+(\text{CH}_4)_{1-6}$,⁹ and $\text{Fe}^+(\text{CH}_4)_{1-4}$.¹⁰

The binding energies of $\text{Cu}^+(\text{CH}_4)$ and $\text{Ag}^+(\text{CH}_4)$ complexes have not been previously measured. There are a few calculations on $\text{Cu}^+(\text{CH}_4)_n$, but they are quite old and use basis sets that are small by modern standards. Musaev calculated the Cu^+-CH_4 binding energy to be 5800-6700 cm^{-1} at the SCF level, depending on the basis set, and 9300 cm^{-1} at the MP2 level. He

obtained a $\text{Cu}^+(\text{CH}_4)\text{-CH}_4$ binding energy of 3500 cm^{-1} at the SCF level.¹¹ Hill *et al.* calculated $\text{Cu}^+\text{-CH}_4$ binding energy to be 5176 cm^{-1} using the SCF based modified coupled pair functional (MCPF) method with Watchers basis set plus two diffuse p functions and a diffuse d function for Cu^+ and a valence double zeta basis for C and H.¹² Later, Maitre and Bauschlicher calculated the binding energy of $\text{Cu}^+\text{-CH}_4$ at the MP2 level with several basis sets as 5900 cm^{-1} to 7500 cm^{-1} .¹³ Vibrational spectroscopy can provide information about upper limits to the bond strengths, the number of methane ligands directly bound to the metal, and the coordination of the methane ligands (η^2 or η^3). In this study, we report vibrational spectroscopy of $\text{Cu}^+(\text{CH}_4)_{1-6}$ and $\text{Ag}^+(\text{CH}_4)_{1-6}$ measured via photofragment spectroscopy. Experimental results are compared to calculated spectra of candidate structures to identify the geometry of the complexes.

5.2 Experimental and Computational Methods

The $\text{M}^+(\text{CH}_4)_n$ ($\text{M}=\text{Cu}, \text{Ag}; n=1\text{-}6$) clusters are generated by laser ablation of a copper or silver rod in an expansion gas mixture of methane in helium at $\sim 50\text{-}100$ psi backing pressure. Mixes containing $\sim 0.1\text{-}1\%$ methane are used to produce $n=1$ and 2 clusters, and more concentrated mixes with $\sim 5\text{-}20\%$ methane are used for larger clusters ($n=3\text{-}6$). The photodissociation spectrum is obtained by taking the ratio of fragment to parent signal and normalizing to laser power as a function of laser wavelength. For these vibrational spectroscopy studies, a wavelength range of $2500\text{-}3100\text{ cm}^{-1}$ was scanned with a Nd:YAG pumped OPO/OPA laser. This produces approximately 5 mJ per pulse near 3000 cm^{-1} , with a line width of 1.8 cm^{-1} . The IR laser is calibrated using the absorption spectrum of methane gas.¹⁴

The $\text{Cu}^+(\text{CH}_4)_n$ and $\text{Ag}^+(\text{CH}_4)_n$ clusters with $n=1,2$ have dissociation energies of $>5000\text{ cm}^{-1}$, so photodissociation requires absorption of more than one photon. To measure spectra of these molecules, two techniques were investigated. The first method, infrared multiple-photon

dissociation spectroscopy (IRMPD), was previously used to measure spectra of $\text{Fe}^+(\text{CH}_4)_n$ ($n=1,2$).¹⁰ The IRMPD of $\text{Cu}^+(\text{CH}_4)_{1-2}$ leads to no dissociation. Therefore, Argon-tagging¹⁵⁻¹⁹ was used to measure the spectra of $\text{Cu}^+(\text{CH}_4)_{1,2}$. This method was also used to measure spectra of $\text{Co}^+(\text{CH}_4)_{1,2}$ and $\text{Ni}^+(\text{CH}_4)_{1,2}$. The advantages and disadvantages of Ar tagging are discussed in the previous chapter. The IRMPD of $\text{Ag}^+(\text{CH}_4)_{1-2}$ is observed, with fairly high dissociation yield, but relatively broad features. Unfortunately, we have failed to produce enough $\text{Ag}^+(\text{CH}_4)(\text{Ar})$ to measure its spectrum. Thus, for $\text{Ag}^+(\text{CH}_4)_{1-2}$ we provide only IRMPD results.

For Cu^+ complexes, calculations were carried out using both the B3LYP and CAM-B3LYP hybrid density functional with the 6-311++G(3df,3pd) basis set²⁰ using the Gaussian 09 program package.²¹ In general, both methods provide the same vibrational frequencies (with a slightly different scaling factor) but the CAM-B3LYP functional provides slightly larger binding energies since it also includes long range interactions. Throughout this chapter, we will refer to CAM-B3LYP binding energies, unless otherwise specified. For the vibrational spectra of the Cu^+ complexes, the same scaling factor that is derived for Co and Ni in previous chapter is used (Equation 4-1).

For Ag^+ , the 6-311++G(3df,3pd) basis set does not exist. Therefore, calculations for Ag^+ complexes use the aug-cc-pVTZ basis with an effective core potential (ECP) on Ag^+ and 6-311++G(3df,3pd) on C and H atoms. Calculations with this new basis set require a new scaling factor. Ideally, this should be done by calculating Co^+ and Ni^+ complexes with this basis set and fitting the new scaling factor for this basis set as in section 4.2 for the 6-311++G(3df,3pd) basis. This will require a lot more calculations for Co^+ and Ni^+ , which have a large number of different isomers and states. Alternatively, we can calculate structures and frequencies for $\text{Cu}^+(\text{CH}_4)_n$ ($n=1-4$) using both aug-cc-pVTZ and 6-311++G(3df,3pd) basis sets to derive a scaling factor for aug-cc-pVTZ basis. To do this, we first convert calculated 6-311++G(3df,3pd) frequencies to

predicted frequencies using equation 4-1. The scaling factor is the ratio of this predicted frequency to the calculated, aug-cc-pVTZ frequency. We then fit a plot of scaling factor vs calculated frequency to obtain:

$$\text{Scaling factor (aug-cc-pVTZ)} = 0.959 - 4.81 \times 10^{-5} \times (3131 \text{ cm}^{-1} - \nu) \quad 5-1$$

This scaling factor is used for the $\text{Ag}^+(\text{CH}_4)_{1-6}$ complexes.

5.3 Results and Discussion

Vibrational spectra of $\text{Ag}^+(\text{CH}_4)_{1-6}$, $\text{Cu}^+(\text{CH}_4)_n$ and $\text{Cu}^+(\text{CH}_4)_m (\text{Ar})_{3-m}$ ($n=3-6$; $m=1,2$) in the C-H stretching region measured using photofragment spectroscopy are shown in Figure 5.1. The experimental peak positions and their relative intensities are presented in Table 5-2. The spectra of the $\text{Cu}^+ - \text{CH}_4$ complexes look similar to those of Co^+ and Ni^+ , but are generally less complex. The small clusters show large red shifts and the peak pattern characteristic of η^2 methane coordination with very strong $\text{M}^+ - \text{CH}_4$ interaction. For bigger clusters the red shift decreases. Spectra of the large, $n=5, 6$, clusters show greatly enhanced intensity in the free C-H stretching region ($2900\text{-}3000 \text{ cm}^{-1}$). The spectra of $\text{Ag}^+(\text{CH}_4)_n$ are quite simple. For smaller clusters with $n < 4$, the spectra consist of a single, broad, asymmetric peak which blue shifts with the cluster size (coming close to the free C-H region). Clusters with $n=5$ and 6 again. The spectra for each cluster will be discussed in detail and assigned in the next section.

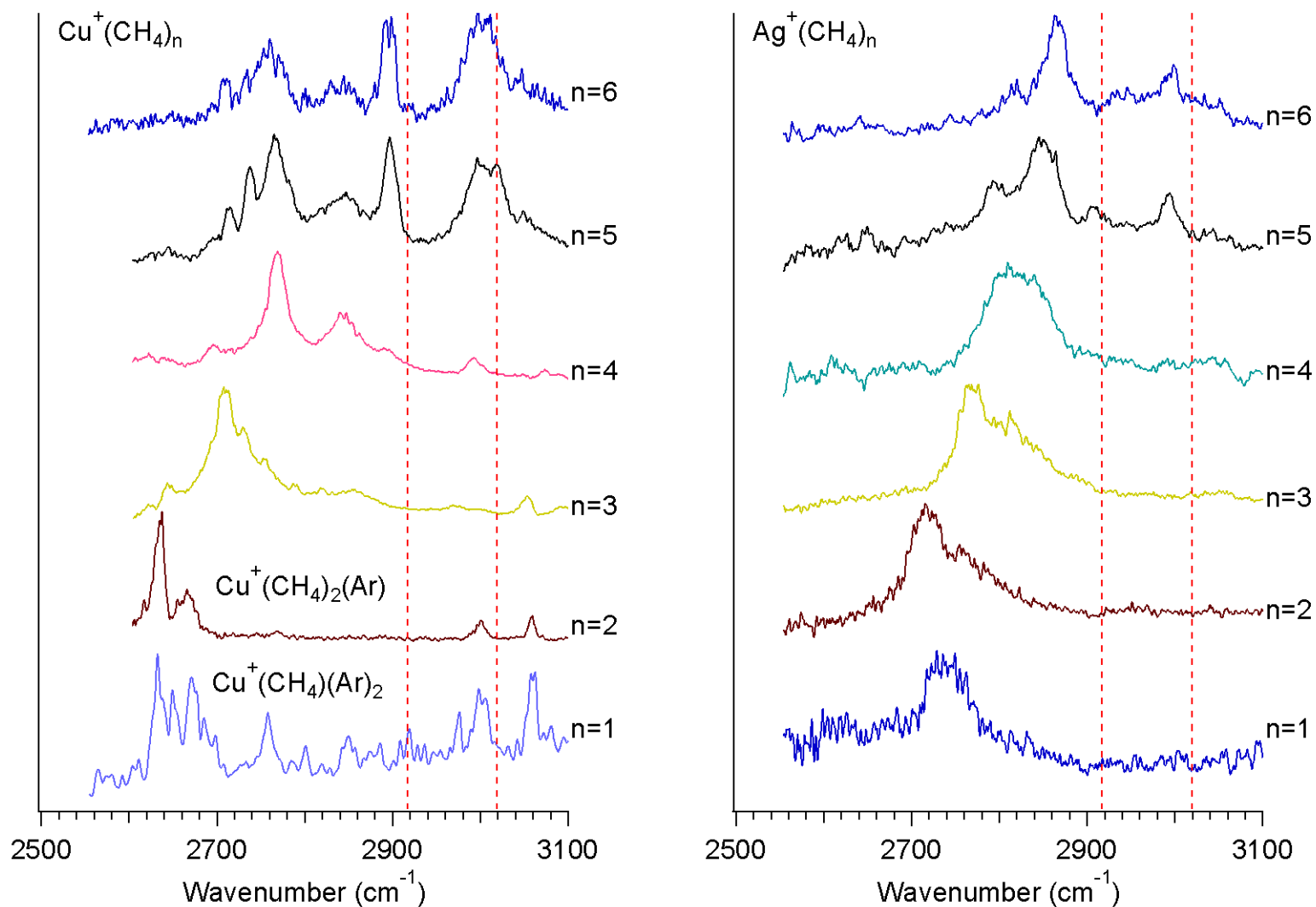


Figure 5.1 Vibrational spectra of $\text{Cu}^+(\text{CH}_4)_{3-6}$, $\text{Cu}^+(\text{CH}_4)_m(\text{Ar})_{3-m}$ (left) and $\text{Ag}^+(\text{CH}_4)_n$ ($n=3-6$; $m=1,2$) (right) in the C-H stretching region (2500–3100 cm⁻¹). The dashed vertical lines show the bare CH₄ symmetric ($\nu_1=2917 \text{ cm}^{-1}$) and antisymmetric ($\nu_3=3019 \text{ cm}^{-1}$) stretches. The y axis shows the normalized and scaled photofragment yield.

5.3.1 Bare and Ar-tagged $M^+(\text{CH}_4)$

As with Co^+ and Ni^+ , using IRMPD, no photodissociation was observed for $\text{Cu}^+(\text{CH}_4)$. In contrast, IRMPD occurred for $\text{Ag}^+(\text{CH}_4)$ with relatively high, 5%, dissociation yield. Not observing photodissociation for $\text{Cu}^+(\text{CH}_4)$ is not surprising, as the Cu^+-CH_4 binding energy is calculated to be $>8000\text{ cm}^{-1}$ (Table 5-1). On the other hand, the Ag^+-CH_4 binding energy, calculated as 5683 cm^{-1} (Table 5-1) is similar to that of Fe^+-CH_4 , measured by Schultz *et al.*²² and Zhang *et al.*²³ as $4760\pm250\text{ cm}^{-1}$ and 6120 cm^{-1} . In our previous study¹⁰ the spectrum of $\text{Fe}^+(\text{CH}_4)$ was obtained by IRMPD. In addition, no dissociation was observed for $\text{Cu}^+(\text{CH}_4)(\text{Ar})$. This is due to its high argon binding energies, calculated to be $>4234\text{ cm}^{-1}$.

Figure 5.2 shows the IR photodissociation spectra of $\text{Cu}^+(\text{CH}_4)(\text{Ar})_2$, taken by monitoring Ar loss, and IRMPD of $\text{Ag}^+(\text{CH}_4)$ taken by monitoring CH_4 loss. The $\text{Cu}^+(\text{CH}_4)(\text{Ar})_2$ spectrum consists of peaks at 2632 and 2757 cm^{-1} , with weaker features at 3000 and 3061 cm^{-1} . This is characteristic of a η^2 methane complex. The two low-frequency vibrations are due to the symmetric and antisymmetric C-H stretches of the proximate hydrogens, respectively. The large red shift reflects weakening of these C-H bonds by the strong $\text{Cu}^+-\text{methane}$ interaction. The weak high-frequency features are due to the symmetric and antisymmetric distal C-H stretches. These show little shift from the antisymmetric stretch in bare CH_4 . The vibrational spectrum of $\text{Ag}^+(\text{CH}_4)$ is very different from that of the copper complex. It consists of a single broad, peak at 2738 cm^{-1} with 50 cm^{-1} full width at half maximum (fwhm).

Table 5-1 Experimental and Calculated 0 Kelvin Binding Energies (in cm^{-1}) of $\text{M}^+(\text{CH}_4)_{n-1}-$
 (CH_4) and $\text{Cu}^+(\text{CH}_4)_n(\text{Ar})_{m-1}-\text{Ar}$ ($\text{M}=\text{Cu}, \text{Ag}$; $n=1-6$; $m=1-2$). The basis set is 6-311++G(3df,3pd) for
Cu, H, C, and Ar and aug-cc-pVTZ (with ECP) for Ag.

	M=Cu		M=Ag	
	B3LYP	CAM-B3LYP	B3LYP	CAM-B3LYP
M^+-CH_4	8001	8473	5132	5460 ^b
$\text{M}^+(\text{CH}_4)-\text{Ar}$	4234	4692	-	-
$\text{M}^+(\text{CH}_4)(\text{Ar})-\text{Ar}$	870	1185	-	-
$\text{M}^+(\text{CH}_4)-\text{CH}_4$	7627	8261	4884	5387 ^b
$\text{M}^+(\text{CH}_4)_2-\text{Ar}$	317	546	-	-
$\text{M}^+(\text{CH}_4)_2-\text{CH}_4$	1487	1943, <2708 ^a	1506	1847, <2768 ^a
$\text{M}^+(\text{CH}_4)_3-\text{CH}_4$	268	585, <2631 ^a	996	1267 ^b
$\text{M}^+(\text{CH}_4)_4-\text{CH}_4$	210	352 ^b	247	529 ^b
$\text{M}^+(\text{CH}_4)_5-\text{CH}_4$	57	170 ^b	32	165 ^b

^a experimental, this work; ^b Geometry and zero-point energy at the B3LYP level

Table 5-2 Experimental and predicted peak positions (cm^{-1}) and their relative intensities of Cu^+ -methane and Ag^+ -methane complexes

	M=Cu	M=Ag
$\text{M}^+(\text{CH}_4)$	2593*, 2699*, 2989*, 3056*	2738(s)
$\text{M}^+(\text{CH}_4)(\text{Ar})_2$	2632(w)**, 2757(vw), 3000(mw), 3061(mw)	-
$\text{M}^+(\text{CH}_4)_2(\text{Ar})$	2637(s), 2665(m), 3000(mw), 3059(mw)	-
$\text{M}^+(\text{CH}_4)_2$	2615*, 2998*, 3058*	2715(s), 2754(sh)
$\text{M}^+(\text{CH}_4)_3$	2644(w), 2707(s), 2730(sh), 2787(sh), 2855(w), 2970(w), 3053(m)	2768(s), 2812(sh)
$\text{M}^+(\text{CH}_4)_4$	2695(w), 2769(s), 2842(m), 2992(m), 3073(w)	2810(s)
$\text{M}^+(\text{CH}_4)_5$	2715(m), 2737(ms), 2765(s), 2846(m), 2896(s), 2996(s), 3018(s), 3048(w,sh)	2793(m), 2849(s), 2906(w), 2993(m)
$\text{M}^+(\text{CH}_4)_6$	2708(m), 2760(m), 2846(m), 2893(s), 2997(s)	2819(m), 2863(s), 2998(m)

*=predicted, s=strong, m=medium, w=weak, vw=very weak, mw=medium weak, sh= shoulder

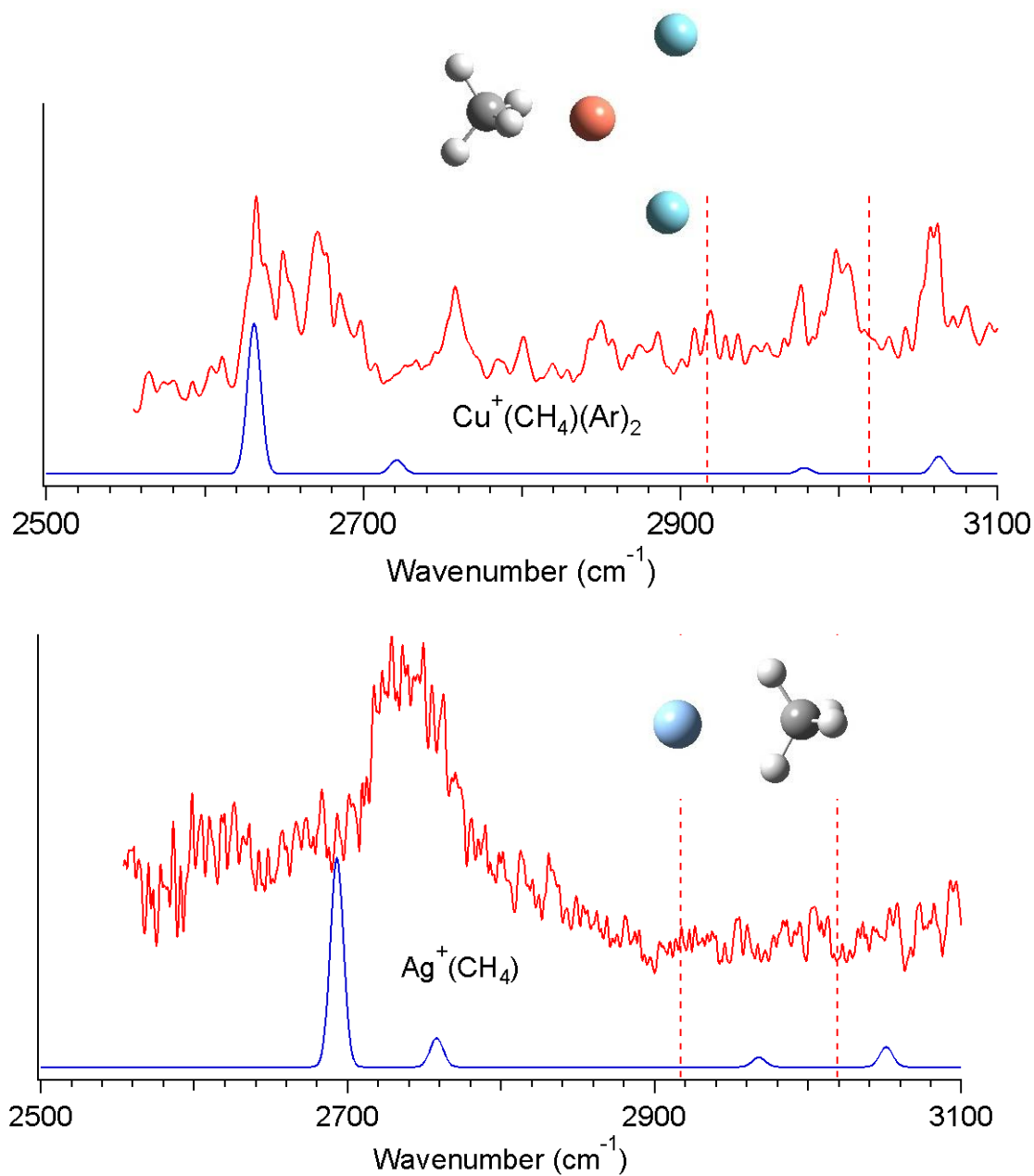


Figure 5.2 Experimental IR photodissociation spectra of $\text{Cu}^+(\text{CH}_4)(\text{Ar})_2$ (top), IRMPD of $\text{Ag}^+(\text{CH}_4)$ (bottom), simulated spectra (blue), and calculated structures. The calculations are carried with the B3LYP functional using the 6-311++G(3df,3pd) basis set for Cu, H, and C and the aug-cc-pVTZ-ECP basis set for Ag. The vertical dashed lines indicate the positions of the C-H stretches in bare CH_4 .

Electronic structure calculations were used to further characterize the observed features and to elucidate the structure of the complexes. Both Cu^+ and Ag^+ have singlet $d^{10}s^0$ ground states and the first excited electronic state lies >2.3 eV above the ground state. Therefore, there is no concern about low lying states – the Cu^+ and Ag^+ clusters have a closed shell, singlet ground state. This makes it much simpler than with Co^+ and Ni^+ where there were many low lying states. One might expect that the structures will have totally symmetric geometries because of the totally symmetric d^{10} occupancy. This is what we observe throughout the spectra of different complexes of Cu^+ and Ag^+ with some minor exceptions. It is noteworthy to mention that although Mn^+ has also a totally symmetric d^5s^1 electronic configuration, its complexes are not totally symmetrical, due to asymmetrically placed ligands increasing the polarization of the 4s orbital.⁹

Earlier studies by both Hill *et al.*¹² and Maitre and Bauschlicher¹³ calculated structures of $\text{Cu}^+(\text{CH}_4)$ to have an η^3 coordinated ground state. However, Maitre also discussed that the basis set they were using is small and when it is increased to include more orbitals it distorts methane coordination towards η^2 . He suggested that pure electrostatic interaction leads to η^3 methane coordination whereas covalency caused by 3d to 4p electron donation favors an η^2 structure. Our calculations, which use the DFT methods (B3LYP and CAM-B3LYP) and a much larger, more flexible basis set, agree with his suggestion and find $\text{Cu}^+(\text{CH}_4)$ to have η^2 methane coordination and C_{2v} symmetry. Indeed, there is not even a local minimum with η^3 methane coordination. An NBO population analysis shows that there is a σ electron donation from $3dz^2$ orbitals (a_1) of Cu to empty a_1 anti-bonding orbitals of CH_4 of $\sim 0.04e^-$ and there is a σ back donation from the a_1 component of the t_2 bonding orbitals of CH_4 to the empty 4s orbital of Cu^+ of $\sim 0.1e^-$. This supports the idea of covalency that is involved in the Cu^+-CH_4 interaction, resulting in η^2 methane coordination. The calculated Cu^+-C bond distance is 2.182 Å.

In $\text{Cu}^+(\text{CH}_4)(\text{Ar})$, the argon atom binds opposite to the methane, forming a C_{2v} complex. The $\text{Cu}^+(\text{CH}_4)\text{-Ar}$ bond strength is calculated to be 4692 cm^{-1} (CAM-B3LYP), which is still too high for one photon dissociation. This energy is even larger than in corresponding Ni and Co complexes, where we did not see any photodissociation. In $\text{Cu}^+(\text{CH}_4)(\text{Ar})_2$ the second argon atom binds to the metal in a trigonal C_s geometry (nearly C_{2v}), in which the argons and proximate hydrogens are not in the same plane (staggered). For the Ar_2 -tagged complex, the calculated C-H stretching frequencies of the proximate hydrogens are somewhat perturbed from those of $\text{Co}^+(\text{CH}_4)$, blue shifting by 39 and 40 cm^{-1} . The binding energy of the second Ar is calculated to be 1185 cm^{-1} (CAM-B3LYP), which is well below the C-H stretching frequencies.

Figure 5.2 shows the photodissociation spectrum of $\text{Cu}^+(\text{CH}_4)(\text{Ar})_2$ along with calculated and scaled simulation. The calculated and scaled values for the ground state are 2631, corresponding to the observed 2632 cm^{-1} peak, and 2721 cm^{-1} for proximate, experimentally observed at 2757 cm^{-1} , and 2978 and 3063 cm^{-1} for distal C-H stretches. The corresponding experimental frequencies are 3000 cm^{-1} and 3061 cm^{-1} , respectively. By adding the shift between the experimental and calculated C-H stretch frequencies in $\text{Cu}^+(\text{CH}_4)(\text{Ar})_2$ to the calculated frequency of $\text{Cu}^+(\text{CH}_4)$, it is possible to predict the C-H stretches of un-tagged $\text{Cu}^+(\text{CH}_4)$. The proximate C-H stretching frequencies in $\text{Cu}^+(\text{CH}_4)$ are predicted to be 2593 cm^{-1} (symmetric) and 2699 cm^{-1} (antisymmetric), which corresponds to shifts of 324 cm^{-1} and 218 cm^{-1} from the symmetric stretch of bare CH_4 , respectively. These large red shifts are characteristic of a structure with η^2 methane coordination. The distal C-H stretching frequencies are predicted to be 2989 cm^{-1} (symmetric) and 3055 cm^{-1} (antisymmetric). The distal C-H stretches are not affected by argon tagging.

For $\text{Ag}^+(\text{CH}_4)$, no literature data could be found. Our calculations predict that the molecule has C_{2v} symmetry and η^2 methane coordination with $2.511\text{ \AA}$ Ag-C bond length. Figure

5.2 shows the experimental vibrational spectrum (IRMPD) of $\text{Ag}^+(\text{CH}_4)$ along with scaled, simulated spectra of the calculated ground state. The spectrum simply has a broad feature at 2738 cm^{-1} . This broadening is a common problem of the IRMPD technique and has been described in Chapter 2. Unfortunately, this broad peak does not provide detailed information about the symmetric and antisymmetric stretches of proximate C-H bonds. The peak contains contributions from both proximate C-H stretches that are calculated as 2693 cm^{-1} and 2758 cm^{-1} . The spectrum also does not show the distal C-H stretching frequencies that are calculated as 2968 cm^{-1} and 3051 cm^{-1} .

In moving from Co^+ to Ni^+ to Cu^+ the observed red shift in the lowest C-H stretch decreases. Although the effective nuclear charge on the metal increases across the period, which would increase the metal-ligand interaction, this is counteracted by adding electrons to d orbitals which repel the ligand. In moving from Cu^+ to Ag^+ , the ionic radius increases. This leads to a larger metal-ligand distance and weaker interaction, resulting in a substantially smaller red shift.

5.3.2 Bare and Ar-tagged $\text{M}^+(\text{CH}_4)_2$

The $\text{Cu}^+(\text{CH}_4)\text{-CH}_4$ and $\text{Ag}^+(\text{CH}_4)\text{-CH}_4$ binding energies are calculated as 8261 cm^{-1} and 5387 cm^{-1} , respectively (Table 5-1). In each complex, the second methane binds less strongly than the first according to the calculations. However, this may not be correct since DFT calculations always tend to overestimate first CH_4 binding energy. This common problem of DFT has been previously discussed for Co^+ and Ni^+ .²³⁻²⁵ For Cu^+ , experimentally, this can be qualitatively justified with the production of much more $n=2$ complexes than $n=1$ in our ion source. This does not hold for Ag^+ where ion yield decreases monotonically with n . In addition, no IRMPD was observed for $\text{Cu}^+(\text{CH}_4)_2$, so its vibrational spectrum is measured by Ar-tagging.

The $\text{Cu}^+(\text{CH}_4)_2\text{-Ar}$ binding energy is calculated to be only 546 cm^{-1} . On the other hand, photodissociation occurs for $\text{Ag}^+(\text{CH}_4)_2$. The yield is $\sim 20\%$, which would be very high for IRMPD, which is typically $<5\%$ for molecules this size, in our instrument. The breadth of the spectrum does suggest it is due to IRMPD.

Figure 5.3 shows the photodissociation spectra of $\text{Cu}^+(\text{CH}_4)_2(\text{Ar})$, taken by monitoring Ar loss, and $\text{Ag}^+(\text{CH}_4)_2$, by CH_4 loss. The $\text{Cu}^+(\text{CH}_4)_2(\text{Ar})$ spectrum shows an intense peak at 2637 cm^{-1} , with a medium shoulder at 2665 cm^{-1} and weaker features at 3000 and 3049 cm^{-1} . Since the Ar binding energy is so small, the Ar-tagged complex must be very cold. Therefore, the spectrum is overall very sharp. This spectrum is very similar to that of $\text{Co}^+(\text{CH}_4)_2(\text{Ar})$ and $\text{Ni}^+(\text{CH}_4)_2(\text{Ar})$, albeit with a smaller red shift, suggesting that it also has η^2 methane coordination. The vibrational spectrum of $\text{Ag}^+(\text{CH}_4)_2$ is simple, having a strong and broad peak at 2715 cm^{-1} and a shoulder at 2754 cm^{-1} , both due to the proximate C-H stretches. Comparing to the $n=1$ complex, this peak is red shifted by 23 cm^{-1} . This is quite unusual, as adding ligands to a complex typically *reduces* the red shift. The reason for that behavior is not clear, and is not reproduced by the calculations, which predict a very small blue shift.

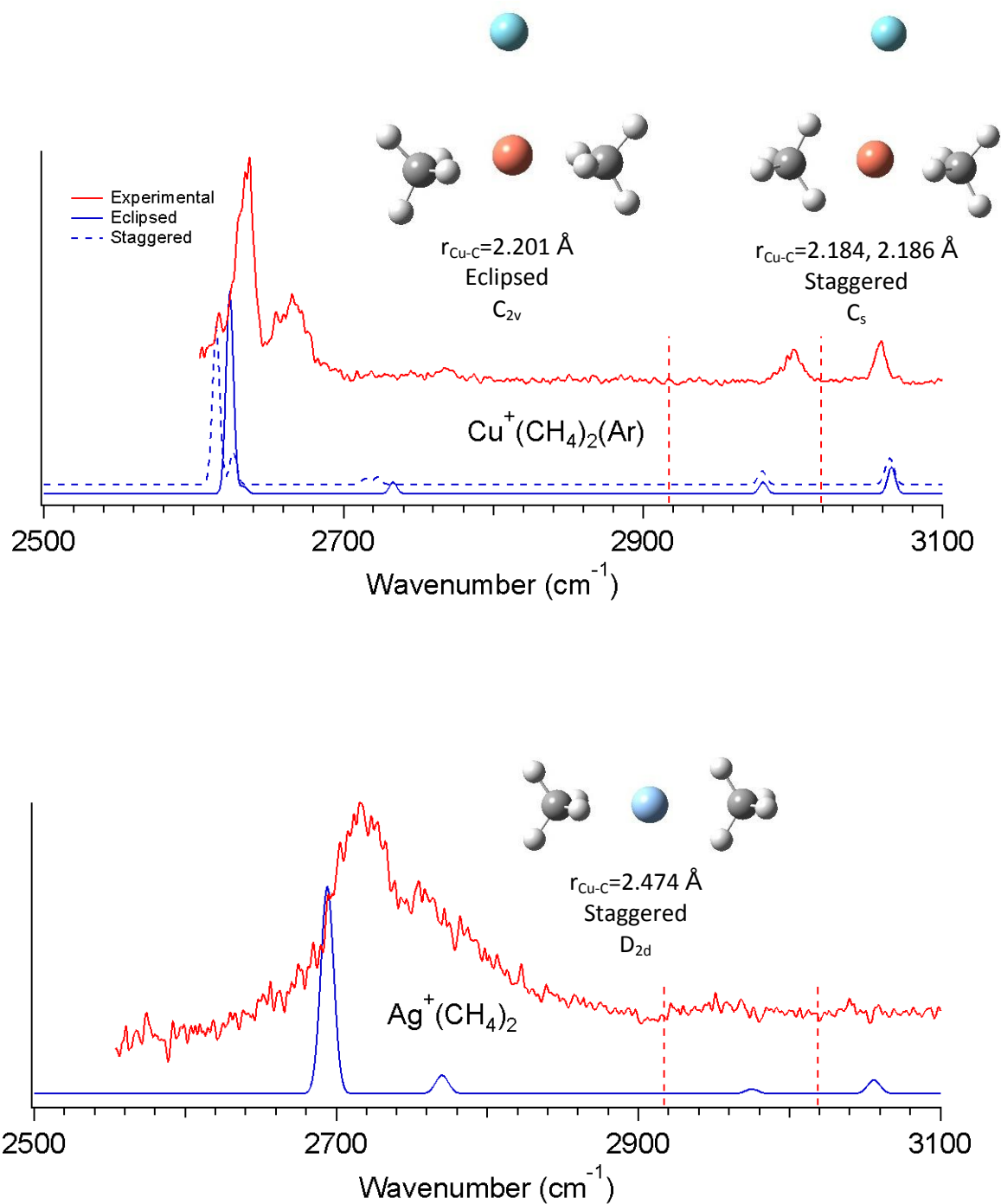


Figure 5.3 Experimental IR photodissociation spectra of $\text{Cu}^+(\text{CH}_4)_2(\text{Ar})$ (top), $\text{Ag}^+(\text{CH}_4)_2$ (bottom), simulated spectra (blue), and calculated structures. The calculations are carried with the B3LYP functional using the 6-311++G(3df,3pd) basis set for Cu, H, and C and the aug-cc-pVTZ-ECP basis set for Ag. The vertical dashed lines indicate the positions of the C-H stretches in bare CH_4 .

There are a few different possible geometries for the $n=2$ complexes. The methane molecules can have η^2 or η^3 coordination, and the ligands can be staggered or eclipsed. Our calculations for $\text{Cu}^+(\text{CH}_4)_2$ and $\text{Ag}^+(\text{CH}_4)_2$ predict that the ground state is η^2 , with C-M-C linear. For copper, we calculate a staggered structure with D_{2d} symmetry and 2.173 Å Cu-C bond length. The D_{2h} eclipsed geometry is not a local minimum and has an imaginary frequency. The calculations predict that $\text{Cu}^+(\text{CH}_4)_2(\text{Ar})$ forms a Tee-shaped complex with 2.201 Å Cu-C bond lengths and a Cu-Ar bond length of 2.922 Å. The four heavy atoms and the distal hydrogens are all in the same plane and the C-Cu-C angle is distorted from 180° to 166° because of the Ar. In addition, there is another competing structure lying only 72 cm^{-1} above the ground state in which the proximate hydrogens are staggered. The Cu-C distances are slightly different (2.184 and 2.186 Å), the Cu-Ar distance is 3.234 Å, and the C-Cu-C angle is 171° . The eclipsed and staggered structures have similar vibrational features that are experimentally indistinguishable (Figure 5.3). The eclipsed ground state has the proximate C-H stretches at 2624 cm^{-1} (symmetric) and 2733 cm^{-1} (antisymmetric) and distal C-H stretches at 2980 cm^{-1} (symmetric) and 3066 cm^{-1} (antisymmetric). Argon tagging is predicted to lead to a small change in the C-H stretches: those from the proximate hydrogens are blue shifted by $19\text{--}23\text{ cm}^{-1}$ while the distal C-H stretches are blue shifted by $1\text{--}2\text{ cm}^{-1}$. Based on the shift between the calculated and experimental frequencies of $\text{Cu}^+(\text{CH}_4)_2(\text{Ar})$, the C-H stretches of un-tagged $\text{Cu}^+(\text{CH}_4)_2$ are predicted to be 2615 cm^{-1} (symmetric) for the proximate hydrogens and 2998 cm^{-1} (symmetric) and 3058 cm^{-1} (antisymmetric) for distal hydrogens. Upon binding to Cu^+ the symmetric C-H stretches of CH_4 red shift by 280 cm^{-1} , confirming that interaction with the metal significantly weakens the C-H bonds in methane.

For $\text{Ag}^+(\text{CH}_4)_2$, we calculate a D_{2d} staggered structure with η^2 coordination and 2.474 Å Ag-C bond lengths. The eclipsed structure has an imaginary frequency and all other initial

geometries such as η^3 and nonlinear C-Ag-C structure converged to the D_{2d} geometry. This is not surprising since the d orbitals are fully occupied, so there is no specific direction that the ligands are restricted. Thus the most symmetrical structure is preferred. The calculated and scaled frequencies are 2694 cm^{-1} (symmetric) and 2770 cm^{-1} (antisymmetric) for the proximate hydrogens and 2975 cm^{-1} (symmetric) and 3056 cm^{-1} (antisymmetric) for the distal hydrogens. There is 21 cm^{-1} difference between the calculated and experimental proximate symmetric C-H frequencies. This might be due to the new scaling factor that is used for Ag complexes.

Comparing $\text{Cu}^+(\text{CH}_4)_2(\text{Ar})$ to the corresponding Co^+ and Ni^+ complexes shows that they are very similar. They all form η^2 complexes, with large red shift of the proximate C-H stretches that gradually decreases from Co^+ to Cu^+ . Structures with the methanes eclipsed and staggered are calculated to have very similar energies and spectra. For $\text{Ag}^+(\text{CH}_4)_2$, the red shift is significantly smaller. The η^2 coordination observed for these metals contrasts with η^3 coordination of $\text{Mn}^+(\text{CH}_4)_2$ and $\text{Fe}^+(\text{CH}_4)_2$.^{9,10}

5.3.3 $\text{M}^+(\text{CH}_4)_3$

The calculated $\text{Cu}^+(\text{CH}_4)_2\text{-CH}_4$ and $\text{Ag}^+(\text{CH}_4)_2\text{-CH}_4$ binding energies are 1943 and 1847 cm^{-1} , respectively (Table 5-1). There is a drastic change in the photodissociation yields for both metal ions from $n=2$ complexes to $n=3$ complexes. The $\text{Cu}^+(\text{CH}_4)_2$ gives no photodissociation whereas $\text{Cu}^+(\text{CH}_4)_3$ gives 20% photodissociation yield. Similarly, $\text{Ag}^+(\text{CH}_4)_2$ gives 20% dissociation while $\text{Ag}^+(\text{CH}_4)_3$ gives 38% yield. Therefore, this observed one photon dissociation gives upper limits to the binding energies of 2708 cm^{-1} for $\text{Cu}^+(\text{CH}_4)_2\text{-CH}_4$ and 2768 cm^{-1} for $\text{Ag}^+(\text{CH}_4)_2\text{-CH}_4$. The binding energies, compared to $n=1$ and 2 complexes, drastically decreased. This decrease is also observed in Ni and Co.

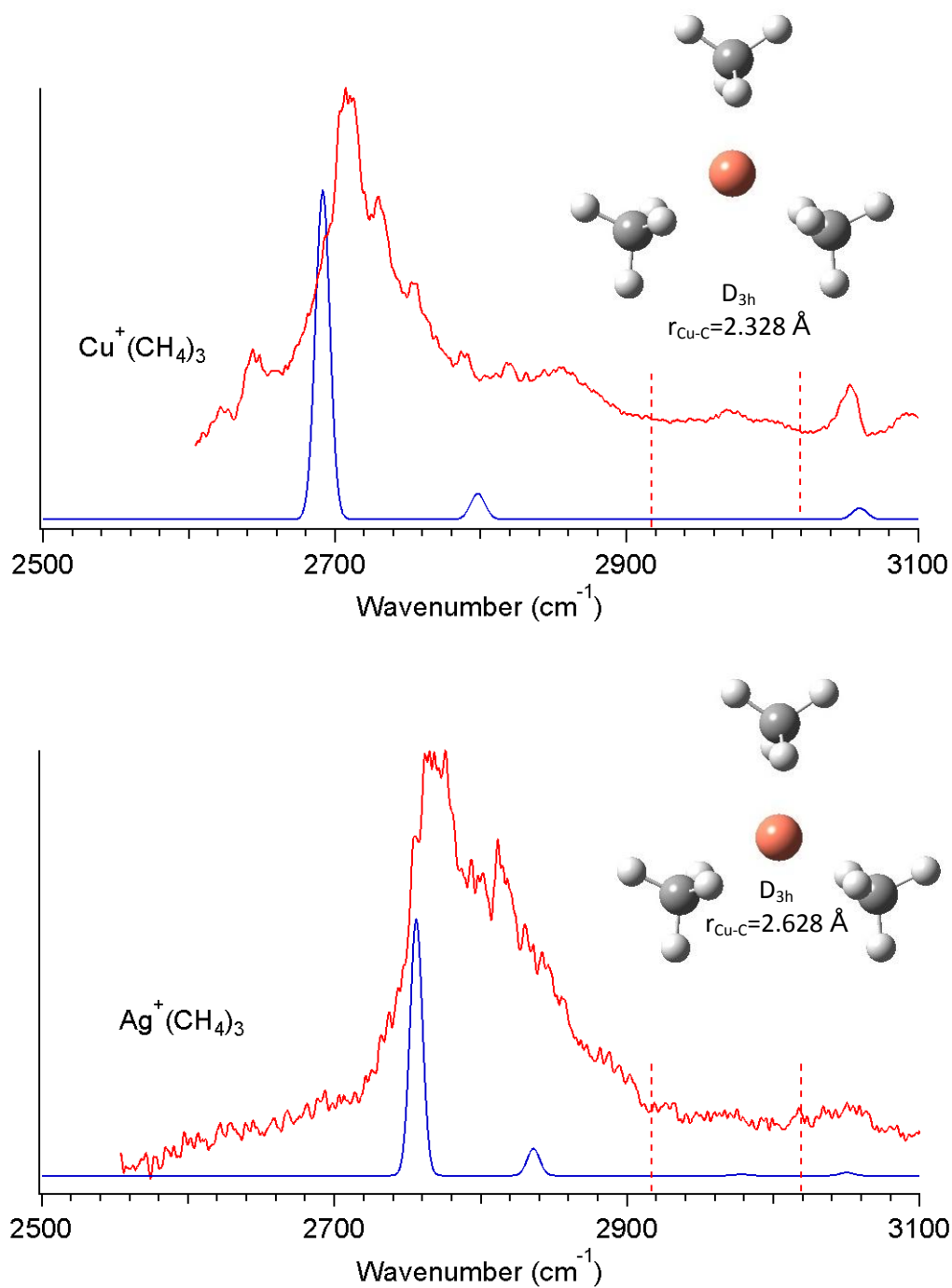


Figure 5.4 Experimental IR photodissociation spectra of $\text{M}^+(\text{CH}_4)_3$ ($\text{M}=\text{Cu}, \text{Ag}$) (red), simulated spectra of the calculated low lying states (blue), and corresponding calculated structures. The vertical dashed lines show the positions of the C-H stretches in bare CH_4 .

Figure 5.4 shows vibrational spectra of $\text{Cu}^+(\text{CH}_4)_3$ and $\text{Ag}^+(\text{CH}_4)_3$. Both losses of 1 CH_4 and 2 CH_4 are observed, and the two channels give similar spectra. Since CH_4 loss (19% for Cu and 37% for Ag) has larger dissociation yield than 2 CH_4 loss ($\sim 1\text{-}2\%$ for both Cu and Ag), the spectra reported here are measured by monitoring the CH_4 loss channel. The copper and silver spectra are similar overall. The $\text{Cu}^+(\text{CH}_4)_3$ spectrum consists of a large peak at 2707 cm^{-1} with shoulders at 2644 cm^{-1} (weak), 2730 cm^{-1} , 2755 cm^{-1} and 2787 cm^{-1} in the proximate C-H stretching region, and typical distal C-H stretches at 2970 cm^{-1} (weak) and 3053 cm^{-1} (medium). The large number of peaks in the proximate C-H stretching region is not clearly understood. There are a few logical considerations for observation of multiple shoulders. First, one might think that these multiplets are from the rotational structure. This is unlikely because the rotational spacing for such a molecule should be very small ($\sim 2\text{-}3\text{ cm}^{-1}$) whereas the observed peaks are separated by more than 20 cm^{-1} . Second, there might be some other isomers present. We have tried calculations considering several possible structures, but they all converge to a D_{3h} equilateral triangular geometry. These shoulders could also be due to combination bands and overtones of H-C-H bends. They can mix with and borrow intensity from C-H stretches. This has been observed for $\text{F}^-(\text{CH}_4)$.²⁶ Another possible reason for these shoulders is that they are due to the combination bands of C-H stretches with hindered methyl rotations (torsion). This has previously been observed for $\text{Cu}^+(\text{H}_2\text{O})(\text{Ar})_n$ complexes.²⁷ The vibrational spectrum of $\text{Ag}^+(\text{CH}_4)_3$ shows a very intense and broad peak at 2768 cm^{-1} with a shoulder at 2812 cm^{-1} . The non-presence of distal C-H stretches (too weak to observe) and stronger, highly red shifted proximate C-H stretches suggest these complexes have η^2 coordination.

Our calculations on $\text{Cu}^+(\text{CH}_4)_3$ identify only one state: an equilateral triangular-shaped structure with D_{3h} symmetry in which the methane ligands are trigonal planar. All three of the ligands have η^2 coordination, and the proximate hydrogens are perpendicular to the plane

containing the heavy atoms. The Co-C bond lengths are 2.328 Å. Figure 5.4 shows calculated, scaled vibrational spectra of $\text{Cu}^+(\text{CH}_4)_3$. This structure is highly symmetrical, so the spectrum is very simple, with the proximate C-H stretches at 2865 cm^{-1} (symmetric) and 2797 cm^{-1} (antisymmetric). The calculated frequencies are shifted from the experiment by $7\text{--}15\text{ cm}^{-1}$.

As with $\text{Cu}^+(\text{CH}_4)_3$, our calculations on $\text{Ag}^+(\text{CH}_4)_3$ identified an equilateral structure with D_{3h} symmetry and 2.628 Å Ag-C bonds. Figure 5.4 shows calculated, scaled vibrational spectra for the equilateral ground state structure of $\text{Ag}^+(\text{CH}_4)_3$. The low lying, strong peak at 2756 cm^{-1} is due to the symmetric stretch of the proximate hydrogens. The corresponding antisymmetric stretch is at 2836 cm^{-1} . The calculated spectrum provides a good match to the broad spectrum observed.

As discussed in Chapter 4, the Co and Ni have also competing Tee shaped structures with similar binding energies to the equilateral triangular structure. We have also considered such structures but they are converged to equilateral triangular structures giving no minimums. The simple $n=3$ spectra observed for the Cu^+ and Ag^+ clusters are in stark contrast to those of their Fe, Co and Ni peers. This reflects the difference between the highly symmetrical structures formed by the d^{10} metals and competing Tee-shaped and distorted equilateral structures found for the d^7 , d^8 , and d^9 metals. Although one might expect that $\text{Mn}^+(\text{CH}_4)_3$ would adopt a symmetrical structure, the three methanes congregate on one side of the metal, polarizing the 4s orbital.⁹

5.3.4 $\text{M}^+(\text{CH}_4)_4$

Our calculated binding energies for $\text{Cu}^+(\text{CH}_4)_4$ and $\text{Ag}^+(\text{CH}_4)_4$ are even lower than for the $n=3$ complexes: 585 cm^{-1} and 1267 cm^{-1} , respectively. It is interesting that the binding energy of $\text{Cu}^+(\text{CH}_4)_{n-1}\text{--CH}_4$ drastically drops from $n=3$ to $n=4$ complex, but does not change a lot for

$\text{Ag}^+(\text{CH}_4)_{n-1}-\text{CH}_4$. Since it is bigger than Cu^+ , Ag^+ can tolerate more ligands in the first shell. As a result the ligands do not repel each other as much in Ag since they are already further apart. Observation of high dissociation yields for the $n=4$ complexes is consistent with these low binding energies.

Figure 5.5 shows vibrational spectra of $\text{Cu}^+(\text{CH}_4)_4$ and $\text{Ag}^+(\text{CH}_4)_4$. Photofragmentation via loss of one to three CH_4 is observed but only 1 CH_4 and 2 CH_4 losses are recorded and they lead to the same spectra. The photodissociation yields for the 1 CH_4 and 2 CH_4 channels are very high: 42% and 25% for Cu and 30% and 10% for Ag. Since the yield for both fragments are so high, we have included the contributions of both fragments in Figure 5.5. The vibrational spectra of both clusters are very simple. The $\text{Cu}^+(\text{CH}_4)_4$ spectrum consists of a weak peak at 2695 cm^{-1} , a relatively narrow (20 cm^{-1} fwhm) and intense peak at 2769 cm^{-1} , along with a medium peak at 2842 cm^{-1} and the typical distal C-H stretches at 2992 cm^{-1} (medium) and 3073 cm^{-1} (weak). The $\text{Ag}^+(\text{CH}_4)_4$ spectrum is dominated by an intense and very broad feature (85 cm^{-1} fwhm) at 2810 cm^{-1} . The simplicity of both spectra suggests that the complexes are highly symmetrical. Both complexes do not show any intense peaks in the distal C-H stretch region, suggesting lack of η^3 methane coordination.

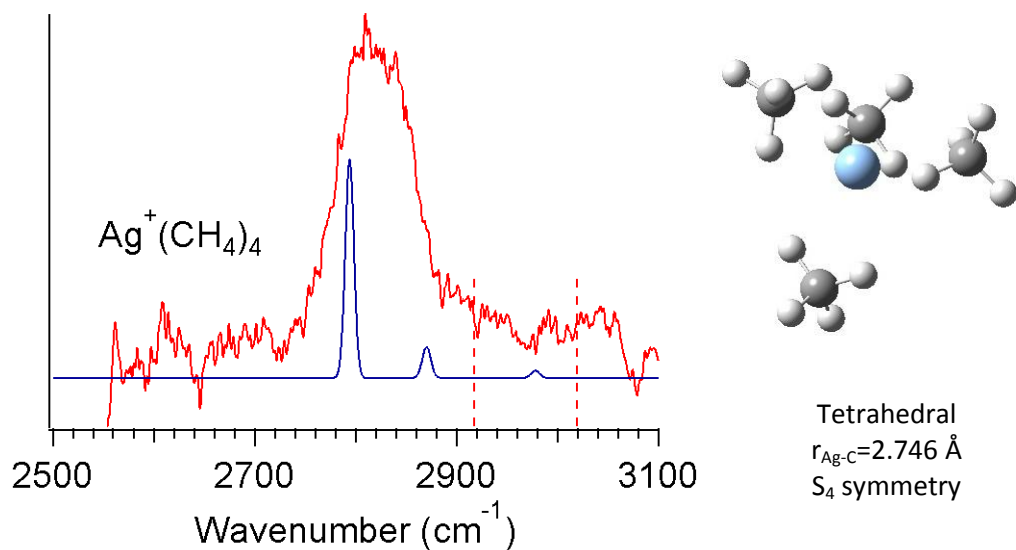
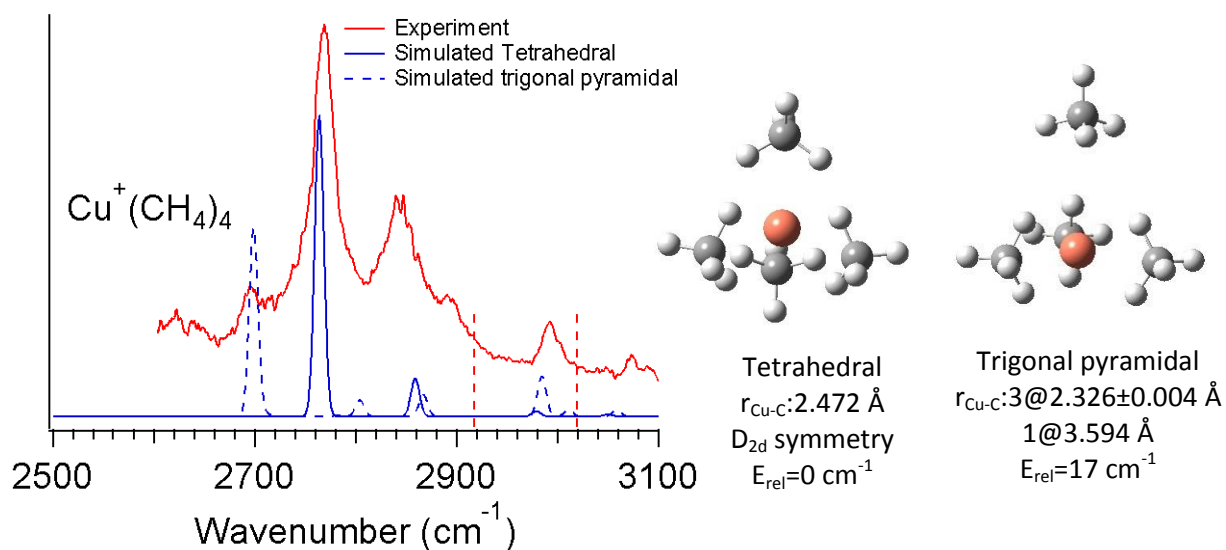


Figure 5.5 Experimental IR photodissociation spectra of $\text{M}^+(\text{CH}_4)_4$ ($\text{M} = \text{Cu}, \text{Ag}$) (red), simulated spectra of the calculated low lying states (blue) and corresponding calculated structures. The vertical dashed lines show the positions of C-H stretches in bare CH_4 .

For $\text{Cu}^+(\text{CH}_4)_4$, we considered four structures: symmetrical square planar and tetrahedral geometries, as well as structures obtained by adding CH_4 to trigonal planar $\text{Cu}^+(\text{CH}_4)_3$, in plane (3+1 structure) and above the metal (trigonal pyramidal). The ground state is a tetrahedral structure with D_{2d} symmetry and 2.472 Å Cu-C bond lengths. The proximate hydrogens have η^2 coordination. However, the trigonal pyramidal structure is calculated to be only 17 cm^{-1} above the ground state. The three CH_4 that form the base of the pyramid are very similar to $\text{Cu}^+(\text{CH}_4)_3$, with η^2 coordination and Cu-C bond lengths of 2.322, 2.327 and 2.330 Å. The apical methane has η^3 coordination, with a much larger Cu-C bond, 3.593 Å. The square planar structure is not stable and distorts to form the fourth structure, which has three CH_4 directly coordinated to Cu^+ (again similar to $\text{Cu}^+(\text{CH}_4)_3$), with Cu-C bond lengths of 2.320 Å. The fourth CH_4 is in the same plane as this core, with η^2 coordination and a Cu-C distance of 4.937 Å. This structure lies 187 cm^{-1} above the ground state. Since the adiabatic binding energy of $\text{Cu}^+(\text{CH}_4)_3\text{-CH}_4$ is only 585 cm^{-1} , this structure is not likely to form. Thus we will not consider this structure further.

Figure 5.5 shows the experimental IR photodissociation spectrum of $\text{Cu}^+(\text{CH}_4)_4$ along with simulated spectra. The simulation belonging to the D_{2d} tetrahedral structure perfectly matches the experimental spectrum. The peak calculated at 2764 cm^{-1} is due to the symmetric stretch of the proximate C-H bonds; the corresponding antisymmetric stretch is the peak at 2860 cm^{-1} . These peaks shift from the experiment only by 6-12 cm^{-1} . The symmetric and antisymmetric stretches of distal C-H bonds are very weak at 2979 cm^{-1} and 3050 cm^{-1} , respectively. In addition, the weak peak observed at 2695 cm^{-1} might be due to the trigonal pyramidal isomer. However, its contribution is small, suggesting that there is only a small barrier between the two isomers.

The situation for $\text{Ag}^+(\text{CH}_4)_4$ is also straightforward (Figure 5.5). Our calculations predict that the ground state is a tetrahedral structure with S_4 symmetry and 2.746 Å Ag-C bond

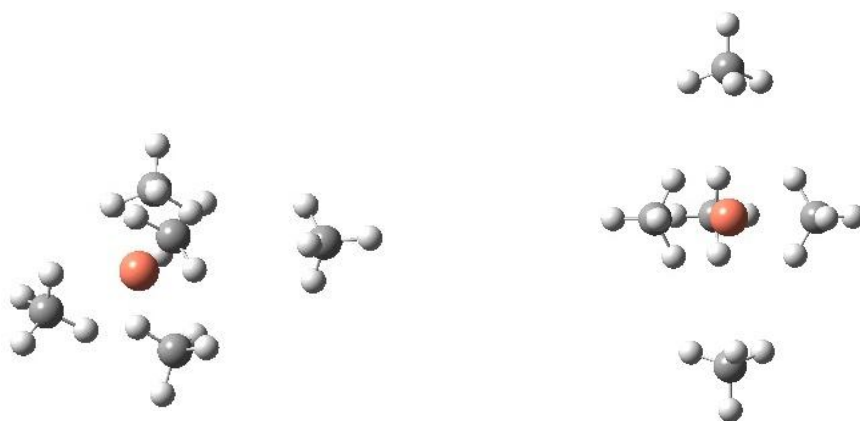
lengths. We also considered a square planar structure, which converged to the tetrahedral geometry. Additionally, we considered the trigonal pyramidal and trigonal planar plus free methane (3+1) structures as they were local minima for the Cu complex. The trigonal pyramidal structure converged to the tetrahedral ground state and the (3+1) structure lies 937 cm^{-1} above the ground state. This structure is at such high energy that it is unlikely to contribute to the spectrum. The calculated spectrum of the tetrahedral ground state is very similar to that of the Cu complex with broader and slightly less red shifted peaks. This is due to the weaker interaction between Ag^+ and CH_4 , which is also observed for the smaller clusters. The calculated spectrum is dominated by the peak at 2795 cm^{-1} , which is due to the symmetric stretch of the proximate hydrogens; the corresponding antisymmetric stretch gives rise to the small peak at 2871 cm^{-1} . The distal C-H stretches are calculated to be very weak. The simulated spectrum of the tetrahedral structure provides an excellent match to the experiment.

The calculated (and observed) structures of $\text{M}^+(\text{CH}_4)_4$ ($\text{M} = \text{Mn, Fe, Co, Ni}$) reflect a competition between two limiting cases: square planar and tetrahedral. The Mn complex has a slightly distorted tetrahedral geometry with η^3 coordinate methanes.⁹ All the other metals have η^2 coordinate $n=4$ complexes. $\text{Ni}^+(\text{CH}_4)_4$ adopts a highly symmetrical square planar structure. The geometry of $\text{Fe}^+(\text{CH}_4)_4$ is similar to that of $\text{Ni}^+(\text{CH}_4)_4$: symmetrical square planar and tetrahedral structures are calculated to be essentially degenerate and both structures contribute to the observed spectrum. In contrast, highly distorted square planar and quasi-tetrahedral structures both appear in the complicated spectrum of $\text{Co}^+(\text{CH}_4)_4$. For Cu, rather than competition between square planar and tetrahedral structures; we observe competition between trigonal pyramidal and tetrahedral geometry. The highly symmetrical tetrahedral structure dominates the observed spectrum. For Ag, we observe only tetrahedral structure.

5.3.5 $M^+(CH_4)_5$

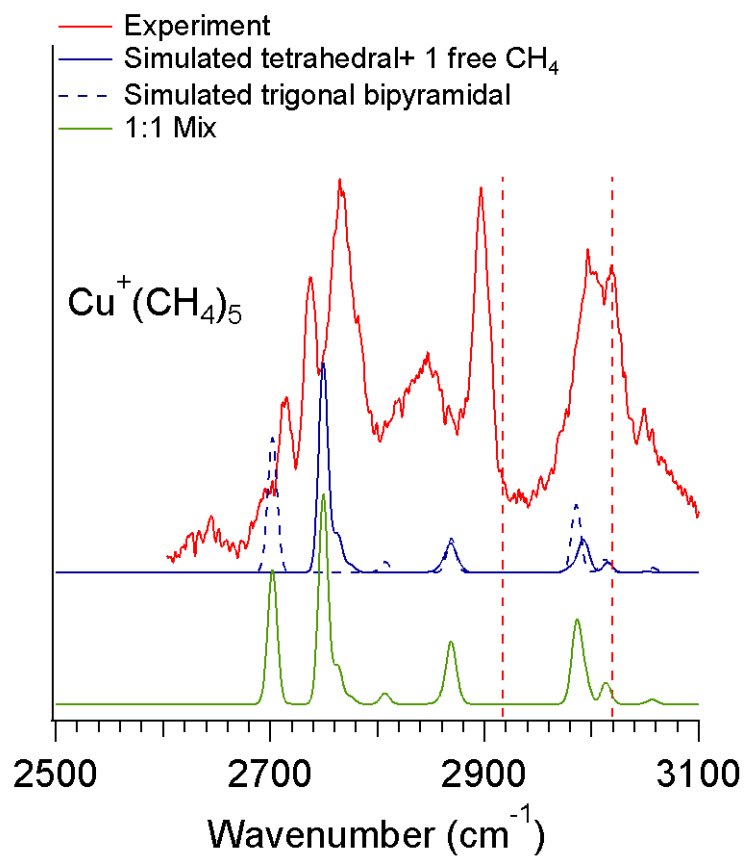
We have calculated the binding energies of $Cu^+(CH_4)_5$ and $Ag^+(CH_4)_5$ to be 352 cm^{-1} and 529 cm^{-1} , respectively. These binding energies are much lower than those of the smaller clusters. They are slightly lower than those measured for $M^+(CH_4)_5$ ($M=Fe, Co, Ni$), $\sim 2\text{ kcal/mol}$ ($\sim 750\text{ cm}^{-1}$),^{23,25} but are larger than the calculated (CCSD(T), extrapolated to the complete basis set limit) methane dimer binding energy of 186 cm^{-1} .²⁸ The binding energies of $Cu^+(CH_4)_n$ are larger than those of $Ag^+(CH_4)_n$ for $n=1,2$; basically the same for $n=3$, and substantially smaller for $n=4-6$. The calculations predict that the binding energy dramatically drops (by a factor of three) at $n=4$ for $Cu^+(CH_4)_n$, while it has a similarly large drop off at $n=5$ for $Ag^+(CH_4)_n$. This suggests that Cu^+ is so small that there is substantial steric repulsion for clusters with $n>3$, while this occurs at $n>4$ for the larger Ag^+ .

Figure 5.6 shows vibrational spectra of $Cu^+(CH_4)_5$ and $Ag^+(CH_4)_5$. Photofragmentation leads to loss of 1 to 3 CH_4 . The photodissociation yields for loss of 2 CH_4 and 3 CH_4 are 50% and 25% for Cu; the yields of loss of 1 to 3 CH_4 are 25%, 15% and 10% for Ag, respectively. All of the channels lead to the same experimental spectra. In each case, the two dominant channels are monitored and the total is incorporated in Figure 5.6. The vibrational spectrum of $Cu^+(CH_4)_5$ is more complex than those of the smaller clusters, implying that the additional CH_4 goes into the second shell. The $Cu^+(CH_4)_5$ spectrum consists of a triplet peaking at 2765 cm^{-1} , a relatively broad and weak feature at 2846 cm^{-1} , a sharp and intense peak at 2896 cm^{-1} and a broad doublet near 3000 cm^{-1} with a shoulder at 3048 cm^{-1} . The $Ag^+(CH_4)_5$ spectrum consists of a medium shoulder at 2793 cm^{-1} , an intense feature at 2849 cm^{-1} and weaker features at 2909 cm^{-1} and 2993 cm^{-1} . In particular, the copper spectrum includes new, intense peaks near the free C-H stretching region, also suggesting that the additional methane ligand is far from the metal ion.



Tetrahedral+1 CH₄
 $r_{\text{Cu-C}}: 2.459, 2.466, 2.466, 2.497 \text{ \AA}$
 $4.466 \text{ \AA}$
 $E_{\text{rel}} = 17 \text{ cm}^{-1}$

Trigonal bipyramidal
 $r_{\text{Cu-C}}: 3@2.328 \text{ \AA}$
 $2@3.680 \text{ \AA}$
 $E_{\text{rel}} = 0 \text{ cm}^{-1}$



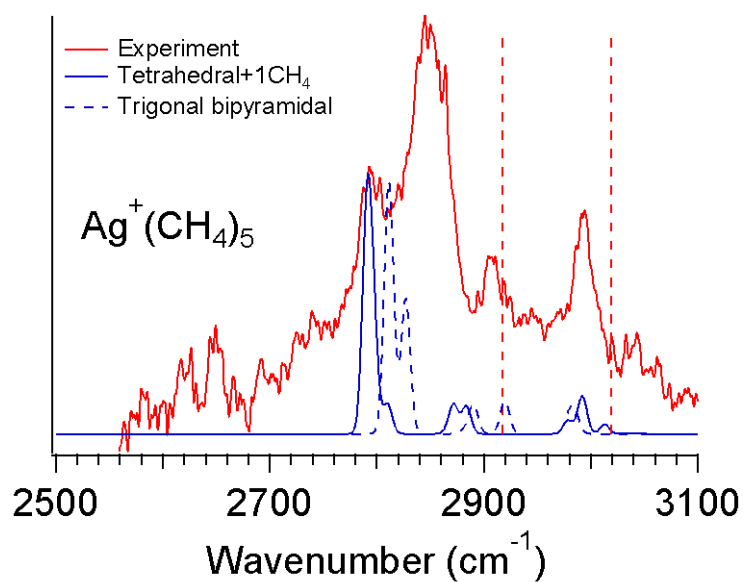
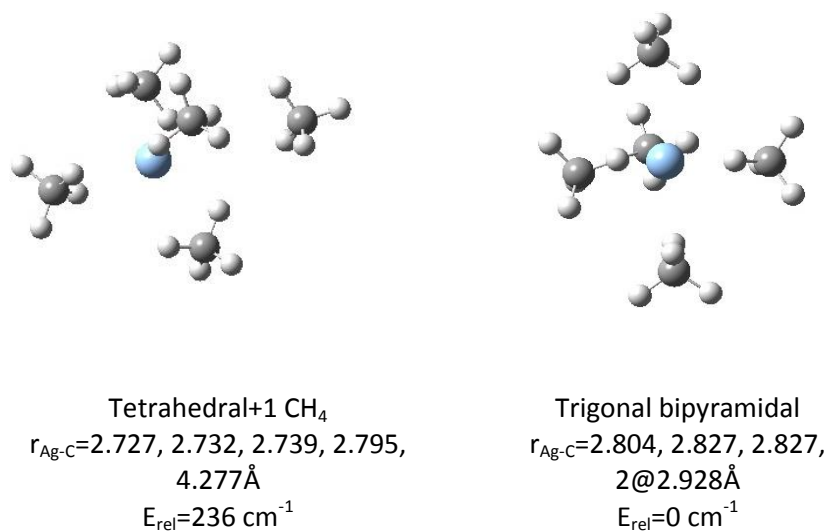


Figure 5.6 Experimental IR photodissociation spectra of $\text{M}^+(\text{CH}_4)_5$ (red) ($\text{M}=\text{Cu}^+, \text{Ag}^+$), simulated spectra of the calculated low lying states (blue) and corresponding calculated structures. The vertical dashed lines show the C-H stretches in bare CH_4 .

For $\text{Cu}^+(\text{CH}_4)_5$, we have considered three structures: trigonal bipyramidal (3+2), tetrahedral + 1 CH_4 (4+1), and square pyramidal. The square pyramidal structure, in which four η^2 coordinate methane molecules form a square planar structure and the fifth η^3 coordinate methane forms the apex of the pyramid, converges to the trigonal bipyramidal coordination. It has been previously shown that square pyramidal and trigonal bipyramidal structures of any molecules can interconvert along a simple reaction coordinate involving two angles.²⁹ Our calculations predict the trigonal bipyramidal structure to be the ground state. It has a three methane core very similar to those of the $n=3$ and 4 complexes, with 2.328 Å Cu-C bond length. These three methane ligands (equatorial) are in η^2 coordination with the proximate hydrogens perpendicular to the trigonal plane. The other two methanes (axial) have η^3 coordination and are much further (3.680 Å) from the metal ion. This structure can be considered as addition of another axial methane to the (3+1) trigonal pyramidal structure. The tetrahedral + 1 CH_4 (4+1) structure is calculated to lie only 245 cm^{-1} above the ground state. It has four η^2 coordinate methane molecules which form the tetrahedral core and an additional η^3 coordinate CH_4 in the second shell, 4.466 Å from the Cu^+ . This additional CH_4 is in the threefold cavity formed by the first-shell methanes in order to minimize repulsion. The first shell methane molecules are similar to those in the $n=4$ complex, but are slightly distorted due to the 5th methane so that the $\text{Cu}^+\text{-C}$ bonds are 2.459, 2.466, 2.466 and 2.497 Å.

Figure 5.6 shows the experimental IR photodissociation spectrum of $\text{Cu}^+(\text{CH}_4)_5$ along with simulated spectra. Although the simulation belonging to the tetrahedral+1 CH_4 (4+1) structure better matches the observed spectrum, the experimental features cannot all be reproduced by either structure alone. The simulation of the (4+1) structure has the strongest peak at 2749 cm^{-1} , which is due to the symmetric proximate C-H stretches of the first shell methanes. The most intense experimental peak, at 2765 cm^{-1} , is assigned to this vibration. The

calculation predicts that in-phase and out-of-phase combinations of this vibration are nearly degenerate. However, in actuality, they might show a larger splitting. This could explain the experimentally observed peaks at 2737 and 2765 cm^{-1} . The shift is only 16 cm^{-1} , which is in the typical range for proximate C-H stretches. The antisymmetric C-H stretches of the proximate hydrogens are calculated at 2868 cm^{-1} . The distal C-H stretches of the inner shell methanes are calculated to be weak. The lone second-shell methane in this structure has a symmetric C-H stretch at 2875 cm^{-1} . The simulations use a Gaussian linewidth of 10 cm^{-1} , so these two peaks overlap; the corresponding experimental peak is at 2896 cm^{-1} . The antisymmetric stretches are calculated at 2990, 2995 and 3015 cm^{-1} , leading to the broad doublet observed near 3000 cm^{-1} .

The trigonal bipyramidal structure also matches some features of the observed spectrum. The symmetric, proximate C-H stretch of the equatorial methanes is calculated to be at 2702 cm^{-1} . This matches the experimental peak at 2715 cm^{-1} . The corresponding antisymmetric stretch is calculated at 2807 cm^{-1} . This could give rise to the broad peak observed at 2846 cm^{-1} . The remaining C-H stretches overlap those of the (4+1) isomer. They are mostly due to the symmetric and antisymmetric stretches of the axial methanes. In Figure 5.6 we show a simulated spectrum of a 1:1 mixture of the two isomers (green trace), which provides a good match to the experiment.

For $\text{Ag}^+(\text{CH}_4)_5$ we have considered the same structures as for the Cu complex: trigonal bipyramidal, tetrahedral + 1 CH_4 (4+1), and square pyramidal. The ground state is found to be a trigonal bipyramidal structure with all the bond lengths similar. The equatorial Ag-C bond lengths are 2.804, 2.827 and 2.827 Å while the axial Ag-C bond lengths are both 2.928 Å. In contrast to the trigonal bipyramidal $\text{Cu}^+(\text{CH}_4)_5$ complex, the proximate hydrogens of the equatorial methanes are in the plane of the equatorial methanes. The (4+1) tetrahedral + 1 CH_4 structure is calculated to lie 236 cm^{-1} higher in energy: the Ag-C bond lengths are 2.727, 2.732,

2.739 and 2.795 Å for the first shell η^2 coordinate methanes and 4.277 Å for the second shell η^3 coordinate methane.

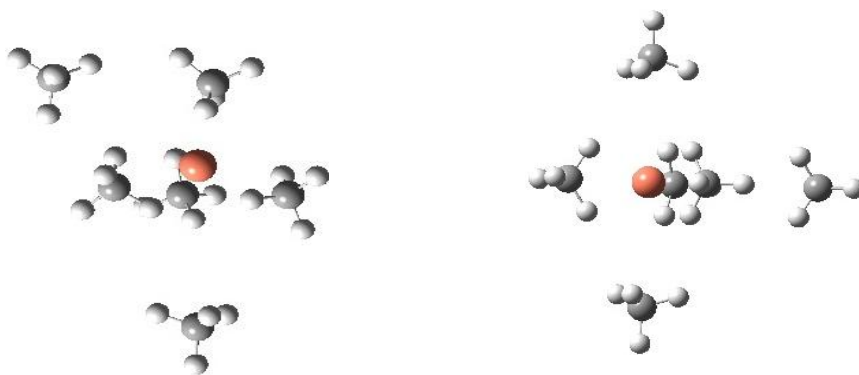
The calculated spectrum of the trigonal bipyramidal structure (Figure 5.6) has an intense peak at 2811 cm^{-1} with a slightly smaller peak at 2827 cm^{-1} . These are due to the proximate C-H stretches of the equatorial and axial methane ligands, respectively. The corresponding antisymmetric stretches are much weaker, at 2890 and 2919 cm^{-1} . The spectrum belonging to the (4+1) isomer shows a very intense peak at 2792 cm^{-1} due to the proximate symmetric C-H stretches of the first shell methanes. As with the corresponding vibration in the Cu complex, the calculations predict that the in-phase and out-of-phase combinations are at very similar energies. These lead to the peak observed at 2793 cm^{-1} . Overlapping transitions from the antisymmetric C-H stretch of inner shell methanes and the symmetric stretch of the outer shell methanes produce the weak doublet near 2878 cm^{-1} . The distal C-H stretches of the inner shell methanes and antisymmetric stretches of the second shell methanes contribute to the peak at 2991 cm^{-1} . The (4+1) structure reproduces the medium experimental peak at 2793 cm^{-1} , but the trigonal bipyramidal structure slightly underestimates the position of the strongest experimental peak at 2849 cm^{-1} . Both isomers contribute to the smaller peaks observed at 2906 and 2993 cm^{-1} .

Previous work on $\text{M}^+(\text{CH}_4)_5$ includes computational work²³ for $\text{M}=\text{Fe}$ and Ni and vibrational spectroscopy and calculations⁹ for $\text{M}=\text{Mn}$. Zhang *et al.* calculated a square pyramidal structure with the apical methane significantly further away from the others for $\text{M}^+(\text{CH}_4)_5$ ($\text{M}=\text{Fe}$ and Ni).²³ The additional methane is added to the ground state structures of the $n=4$ complexes, which they calculated to be square planar. However, it is not clear whether they considered additional structures since their focus was primarily on smaller clusters. However, the possible structures of $n=4$ complexes of Cu are tetrahedral and trigonal pyramidal. Thus, the addition of

methane to these two structures leads to the favored structures for $n=5$: tetrahedral + 1 CH_4 and trigonal bipyramidal. Dryza *et al.*⁹ calculated $\text{Mn}^+(\text{CH}_4)_5$ to have a trigonal bipyramidal structure with all the methanes having η^3 coordination, and the resulting spectrum matches their experiment. Both Cu^+ and Mn^+ have spherical electronic configurations ($3d^{10}$ and $3d^5 4s^1$, respectively), and they might be expected to adopt similar structures. However, Mn^+ interacts very weakly with methane due to the large 4s orbital, so the clusters adopt η^3 methane coordination with long $\text{Mn}^+\text{-C}$ bonds (3.16 Å axial and 3.10 Å equatorial). Because of this long $\text{Mn}^+\text{-C}$ distance, there is little ligand-ligand repulsion and all of the ligands can be in the first shell. The Cu^+ , with smaller 3d orbitals and an empty 4s orbital, interacts much more strongly with methane, so the clusters have η^2 methane coordination with much shorter $\text{M}^+\text{-C}$ bonds. In the trigonal bipyramidal structure, the equatorial bond lengths are so short (2.328 Å) that the axial methanes can only approach to 3.680 Å due to steric effects.

5.3.6 $\text{M}^+(\text{CH}_4)_6$

We have calculated the binding energies of $\text{Cu}^+(\text{CH}_4)_6$ and $\text{Ag}^+(\text{CH}_4)_6$ to be 170 cm^{-1} and 165 cm^{-1} . Zhang *et al.*²³ estimated bond strengths for $\text{M}^+(\text{CH}_4)_6$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}$) to be $\sim 2\text{ kcal/mol}$ (700 cm^{-1}). The calculated binding energies of the larger clusters are expected to be less accurate than for smaller clusters as dispersion forces become increasingly important, and the B3LYP and CAM-B3LYP functionals do not explicitly include dispersion interactions.



Tetrahedral + 2 CH₄

$r_{\text{Cu-C}}: 2@2.454 \text{ \AA}$

$2@2.488 \text{ \AA}$

$2@4.458 \text{ \AA}$

1st shell: $4x\eta^2$

2nd shell: $2x\eta^3$

$E_{\text{rel}}=147 \text{ cm}^{-1}$

Trigonal bipyramidal + 1 CH₄

$r_{\text{Cu-C}}: 3@2.326\pm0.003 \text{ \AA}$

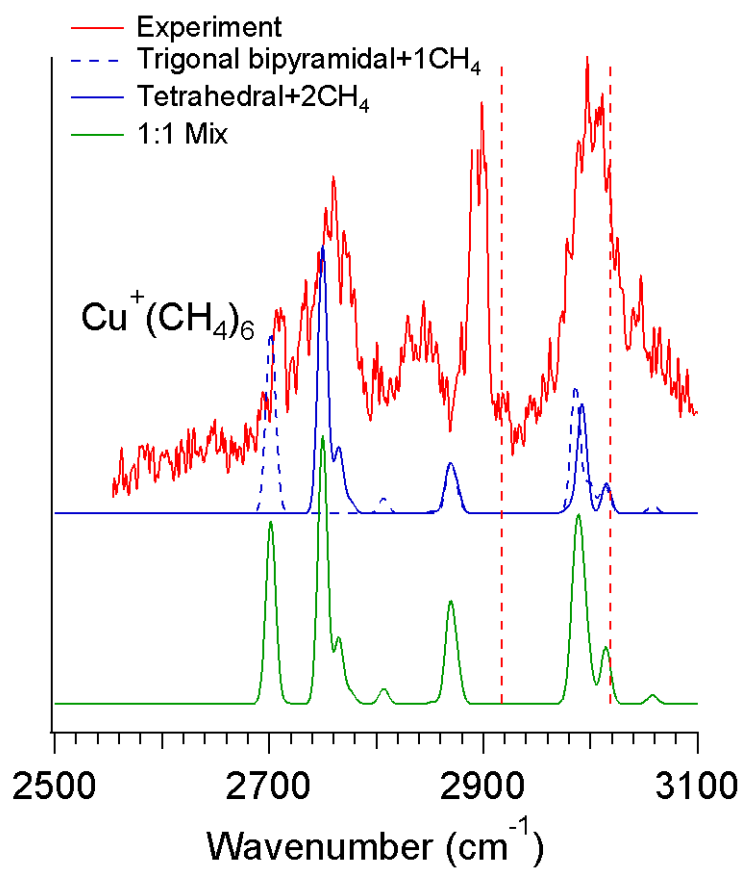
$2@3.695 \text{ \AA}$

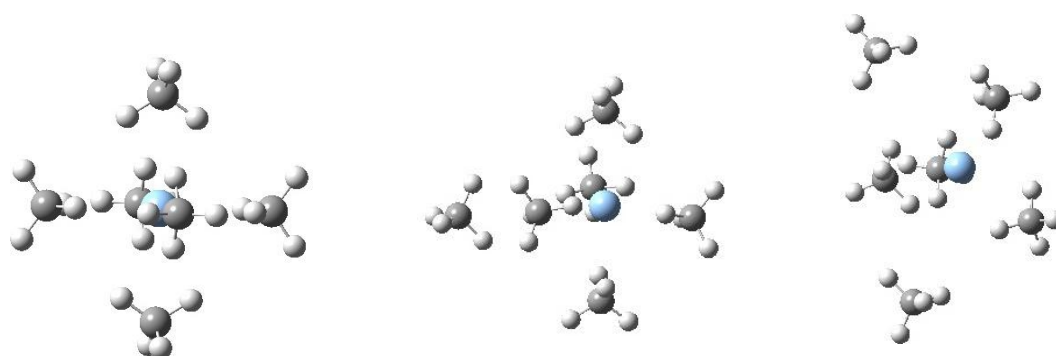
$1@4.974 \text{ \AA}$

1st shell: $3x\eta^2+2x\eta^3$

2nd shell: $1\eta^2$

$E_{\text{rel}}=0 \text{ cm}^{-1}$





Octahedral
 $r_{\text{Ag-C}}=4@2.962 \text{ \AA}$
 $2@2.966 \text{ \AA}$
 T_h symmetry
 1^{st} shell: $4x\eta^2$
 2^{nd} shell: $2x\eta^2$
 $E_{\text{rel}}=101 \text{ cm}^{-1}$

Trigonal bipyramidal+1 CH_4
 $r_{\text{Ag-C}}=2.784, 2.811, 2.850 \text{ \AA}$
 $2.936, 2.941 \text{ \AA}$
 $4.749 \text{ \AA}$
 1^{st} shell: $5x\eta^2$
 2^{nd} shell: $1x\eta^2$
 $E_{\text{rel}}=0 \text{ cm}^{-1}$

Tetrahedral+2 CH_4
 $r_{\text{Ag-C}}=2@2.729 \text{ \AA}$
 $2@2.767 \text{ \AA}$
 $2@4.497 \text{ \AA}$
 1^{st} shell: $4x\eta^2$
 2^{nd} shell: $2x\eta^3$
 $E_{\text{rel}}=83 \text{ cm}^{-1}$

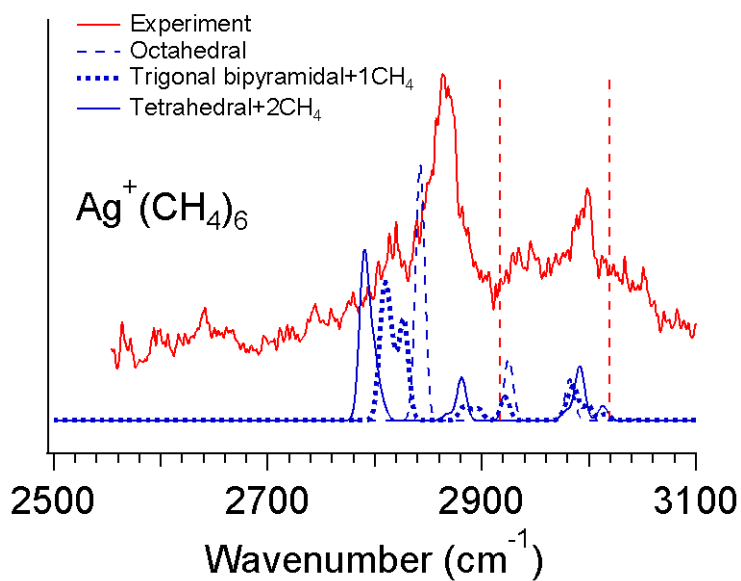


Figure 5.7 Experimental IR photodissociation spectrum of $\text{M}^+(\text{CH}_4)_6$ for $\text{M}=\text{Cu}$ (top), Ag (bottom), simulated spectra of the calculated low lying states (blue) and corresponding calculated structures. The vertical dashed lines are C-H stretches of bare CH_4 .

Figure 5.7 shows vibrational spectra of $\text{Cu}^+(\text{CH}_4)_6$ and $\text{Ag}^+(\text{CH}_4)_6$. Photo-fragmentation by loss of 1 to 3 CH_4 is observed. The photodissociation yields are ~12%, ~25% and ~33% for 1, 2 and 3 CH_4 loss from $\text{Ag}^+(\text{CH}_4)_6$, respectively. Loss of 2 CH_4 and 3 CH_4 are recorded for both Cu and Ag. All of the fragmentation channels lead to the same spectra. The spectra of the $n=6$ complexes are very similar to the corresponding $n=5$ spectra with slightly smaller red shifts. The $\text{Cu}^+(\text{CH}_4)_6$ spectrum consists of a medium and relatively broad peak at 2760 cm^{-1} and two intense peaks at 2893 cm^{-1} and 2997 cm^{-1} . The latter two are very close to bare methane C-H stretches. In addition, there are two weak features at 2708 cm^{-1} and 2844 cm^{-1} . The $\text{Ag}^+(\text{CH}_4)_6$ spectrum is dominated by two peaks at 2863 cm^{-1} and 2998 cm^{-1} . In addition, there is a weak peak at 2819 cm^{-1} .

For $\text{Cu}^+(\text{CH}_4)_6$, we have considered three structures: octahedral, trigonal bipyramidal + 1 CH_4 (3+2+1) and tetrahedral + 2 CH_4 (4+2). The octahedral structure converges to the (3+2+1) structure. It has three η^2 coordinate equatorial methane ligands with nearly the same basic structure as the $n=3$ and $n=5$ complexes, and 2.323, 2.326 and $2.329\text{ \AA}$ Cu-C bond lengths. The axial η^3 coordinate methane molecules are similar to those in the trigonal bipyramidal structure, with $3.695\text{ \AA}$ Cu-C bonds. The 6th CH_4 has η^2 coordination and a long Cu-C bond of $4.974\text{ \AA}$. It is in the equatorial plane and lies in the cavity of two first shell methanes. The proximate hydrogens of the equatorial methane ligands and the sixth methane are perpendicular to the trigonal plane. The second structure, tetrahedral + 2 CH_4 (4+2), is basically formed by addition of two second shell η^3 coordinate methane molecules to the tetrahedral first shell η^2 coordinate methanes in the $n=4$ complex. The Cu-C bond lengths for the first shell methanes are similar to those in the $n=4$ complex: $2.454\text{ \AA}$ (x2) and $2.488\text{ \AA}$ (x2); they are $4.458\text{ \AA}$ for the second shell methanes, similar to that in the tetrahedral + 1 CH_4 (4+1) structure in the $n=5$ complex. Our

calculations predict that the trigonal bipyramidal +1 CH₄ (3+2+1) structure is the ground state, but the (4+2) lies only 147 cm⁻¹ higher in energy.

Figure 5.7 shows the experimental IR photodissociation spectrum of Cu⁺(CH₄)₆ along with simulated spectra. The experimental features are almost completely fit by the tetrahedral + 2 CH₄ (4+2) structure. However, one can find some features from the trigonal bipyramidal + 1 CH₄ (3+2+1) as well. The simulation of the (4+2) structure has the strongest peak at 2750 cm⁻¹, which is due to the proximate hydrogens of the tetrahedral methanes; this is observed at 2760 cm⁻¹. The corresponding antisymmetric stretch is calculated to be at 2869 cm⁻¹ and overlaps the symmetric C-H stretch of the second shell methanes. This corresponds to the experimental peak at 2893 cm⁻¹. The symmetric and antisymmetric distal C-H stretches of the first shell methanes are calculated to not contribute to the spectrum (intensities < 1 km/mol). The antisymmetric proximate C-H stretches of the second shell methanes are calculated to produce the intense, lower frequency peak of the doublet at 2992 cm⁻¹ and the distal C-H stretches are at 3015 cm⁻¹ (the higher frequency peak of the doublet). The experimental peak at 2997 cm⁻¹ is the combination of these two stretches. Although this (4+2) structure mostly covers the experimental peaks, we should note that this structure is calculated to be 147 cm⁻¹ higher in energy than the (3+2+1) structure. The vibrations of the ground (3+2+1) structure also help to explain the observed spectrum. The most intense peak of this structure is calculated to be at 2702 cm⁻¹ and is due to the symmetric proximate C-H stretches of the first shell equatorial methanes. This peak matches the weak experimental peak at 2708 cm⁻¹. The corresponding antisymmetric stretch is at 2807 cm⁻¹, matching the observed broad peak at 2846 cm⁻¹. The rest of the calculated peaks are due to the more distant methanes and overlap those of the (4+2) complex. They give rise to the observed peaks at 2893 and 2997 cm⁻¹. In Figure 5.7 we also include (green) a 1:1 combination of both isomers, which matches the experiment. The strong

peaks observed at 2893 cm^{-1} and 2997 cm^{-1} , are only shifted by $\sim 23\text{ cm}^{-1}$ from the CH_4 symmetric and antisymmetric stretches in bare CH_4 , indicating that these methanes interact very weakly with the metal. Since the sixth methane is so weakly bound, there is almost no red shift for the vibrations when moving from $n=5$ to $n=6$.

For $\text{Ag}^+(\text{CH}_4)_6$ (Figure 5.7), we considered three structures: octahedral, trigonal bipyramidal + 1 CH_4 (5+1), and tetrahedral + 2 CH_4 (4+2). The calculations predict that all of these are stable minima and that they have similar energies. The ground state is predicted to be the (5+1) structure, formed by addition of the sixth methane to the trigonal bipyramidal $\text{Ag}^+(\text{CH}_4)_5$ complex. It has Ag-C bond lengths of 2.784, 2.811, 2.850 (equatorial); 2.936, 2.941 (axial); and 4.749 Å (second shell). All of the methane molecules are in η^2 coordination. The octahedral structure is calculated to lie 101 cm^{-1} higher in energy. It is highly symmetrical (T_h symmetry due to the hydrogens) with almost identical Ag-C bond lengths of 2.962 Å (x4) and 2.966 Å (x2). In this structure, the proximate hydrogens of the opposite methanes are eclipsed and those of neighboring methanes are staggered in order to minimize repulsion. The (4+2) structure is calculated to lie 83 cm^{-1} above the ground state. As in the case of Cu; it is formed by addition of the fifth and sixth methane ligands to the tetrahedral core. The Ag-C bond lengths are 2.772 Å (x2) and 2.725 Å (x2) for the first shell η^2 coordinate methanes and 4.330 Å (x2) for the second shell η^3 coordinate methanes. The tetrahedral structure in the first shell is distorted due to these additional second shell methanes such that the Ag-C bond lengths of the two first shell methanes that are on the same side as the second shell methanes are shortened. This may be explained with the idea of having more electron density on these two first shell methanes because of the outer methanes, thus they are attracted more by the metal. Another factor which may contribute is polarization of the metal 3d orbital so that there is less electron density towards the side with more ligands.

The octahedral structure provides the best match to the experimental spectrum. The most intense peak of the calculated octahedral structure is at 2842 cm^{-1} and is due to the symmetric proximate C-H stretches of the six methanes. This corresponds to the strong 2863 cm^{-1} observed peak. The antisymmetric stretch of this mode is at 2915 cm^{-1} . This might be responsible for the weak peak near 2935 cm^{-1} . The symmetric distal C-H stretches are calculated at 2982 cm^{-1} , corresponding to the observed peak at 2998 cm^{-1} . Although the octahedral structure predicts almost all the features in the experiment, it fails to predict the observed weak peak at the lowest frequency, 2819 cm^{-1} . This feature can be explained by a small contribution from the (5+1) isomer (doublet at 2810 and 2826 cm^{-1}). In addition, the (4+2) structure also predicts a peak at 2791 cm^{-1} , which may also be responsible for the same observed peak, considering the typical differences between observed and calculated frequencies.

For $\text{Fe}^+(\text{CH}_4)_6$ and $\text{Ni}^+(\text{CH}_4)_6$, Zhang *et al.* calculate distorted octahedral structures, with the axial M-C bond lengths substantially (by $\sim 1.6\text{ \AA}$) larger than the equatorial ones.²³ Again this study did not appear to examine all possible structures for these larger clusters, so they may have missed (4+2) and (3+2+1) structures, which are calculated to be the minimum energy structures for $\text{Cu}^+(\text{CH}_4)_6$. For $\text{Mn}^+(\text{CH}_4)_6$, Dryza *et al.* find an octahedral structure, with $3.21\text{ \AA}$ Mn-C bond length and η^3 methane coordination.⁹ This weak interaction and long Mn-C bonds are due to the large singly occupied 4s orbital. For $\text{Ag}^+(\text{CH}_4)_6$, the octahedral, (4+2), and (5+1) structures are calculated to lie at similar energies. In the octahedral structure, the methane ligands have η^2 coordination, with M-C bond lengths substantially shorter than in the Mn complex.

5.4 Summary and Conclusions

In this work, we present vibrational spectra of $\text{Cu}^+(\text{CH}_4)_n$ and $\text{Ag}^+(\text{CH}_4)_n$ ($n=1-6$). Spectra are obtained by photofragment spectroscopy monitoring loss of one or more CH_4 following IR photo-excitation. Calculations predict that the positions and intensities of bands in the C-H stretching region depend strongly on the coordination of the CH_4 to the metal (η^1 , η^2 or η^3) and on the M-C bond length, and thus are sensitive to the number of ligands in the first and second shell. We determine the structures of the complexes by comparing calculated vibrational spectra of low-lying candidate structures to the observed IR photodissociation spectra. The vibrational spectra show that all of the complexes adopt an η^2 methane configuration in the first shell, in accord with theoretical predictions. The binding energies of the $n=1$ and 2 clusters are so high that they require three photons to dissociate, therefore no photodissociation is observed for Cu. The spectra of the argon tagged complexes are measured by monitoring Ar loss. The Ag complexes dissociate via infrared multiple photon dissociation. The spectra of the $n=1-3$ complexes reveal single structures with high symmetry. The observed, spectroscopic, onset of the $\text{Cu}^+(\text{CH}_4)_3$ spectrum provides an upper limit: $D_0(\text{Cu}^+(\text{CH}_4)_2\text{-CH}_4) < 2708 \text{ cm}^{-1}$. The $n=4$ clusters have a competition between trigonal pyramidal and tetrahedral structures for Cu whereas only the tetrahedral structure is observed for Ag. For the $n=5$ Cu clusters, trigonal bipyramidal and tetrahedral + 1 CH_4 structures compete. For Ag, a symmetrical trigonal bipyramidal structure is the ground state, the tetrahedral + 1 CH_4 structure is also observed. For $\text{Cu}^+(\text{CH}_4)_6$, the tetrahedral + 2 CH_4 (4+2) and trigonal bipyramidal + 1 CH_4 structures are observed, with the (4+2) dominating. For Ag, there are three competing structures. The highly symmetrical octahedral structure accounts to the majority of the observed spectrum, but the (5+1) and (4+2) structures may also contribute. Since Cu^+ is smaller than Ag^+ , steric interactions between the methanes play a more important role in determining the stable structure.

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CHAPTER 6

EXTENSIONS AND FUTURE WORK

6.1 $M^+(H_2O)$ Systems

There are several directions in which the studies presented throughout this dissertation can be expanded. The studies that are presented in Chapter 3 for $Co^+(H_2O)$ can be extended to the other late first-row transition metals, Mn, Fe, Ni and Cu.

Our group has studied $Ni^+(H_2O)$ electronic spectroscopy.¹ Because Ni^+ has a d^9 electronic configuration, with only one d orbital hole, it has many fewer excited states than Co^+ , with d^8 electronic configuration and two holes in d orbitals. Figure 6.1 shows the electronic photodissociation spectrum of $Ni^+(H_2O)$. Transitions to two excited states are observed, both of the transitions are due to $3d \rightarrow 4s$ (a parallel and a perpendicular). Similar to $Co^+(H_2O)$, a long vibrational progression due to the metal-ligand stretch is observed. As with cobalt, binding to the metal weakens the O-H bonds in water and increases the H-O-H angle slightly.

Similarly, our group has recently studied $Mn^+(H_2O)$ electronic spectroscopy via photodissociation.² The Mn^+ spectrum is interesting and different from those of Co^+ and Ni^+ . Because Mn^+ has $3d^5 4s^1$ electronic configuration, a $4s \rightarrow 4p$ transition is excited. The $4s \rightarrow 4p_x$ and $4p_y$ are observed to lead to perpendicular bands, while the $4s \rightarrow 4p_z$ would give a parallel band (not observed).

Our group has also attempted to study the electronic spectroscopy of $Cu^+(H_2O)$ complexes. Surprisingly, irradiation of $Cu^+(H_2O)$ over a wide range of wavelengths in the visible and near UV did not lead to photofragmentation.

It would be good to extend these studies to $Fe^+(H_2O)$. Since the ground state of Fe^+ is sextet ($3d^6 4s^1$), and the quartet state ($3d^7$) is energetically very close, it would be very interesting to see how the presence of nearby quartet and sextet states affects the ground and

excited states of the complex. However, this might lead to a very complicated spectrum due to overlapping electronic states and a relatively big spin-rotation interaction term.

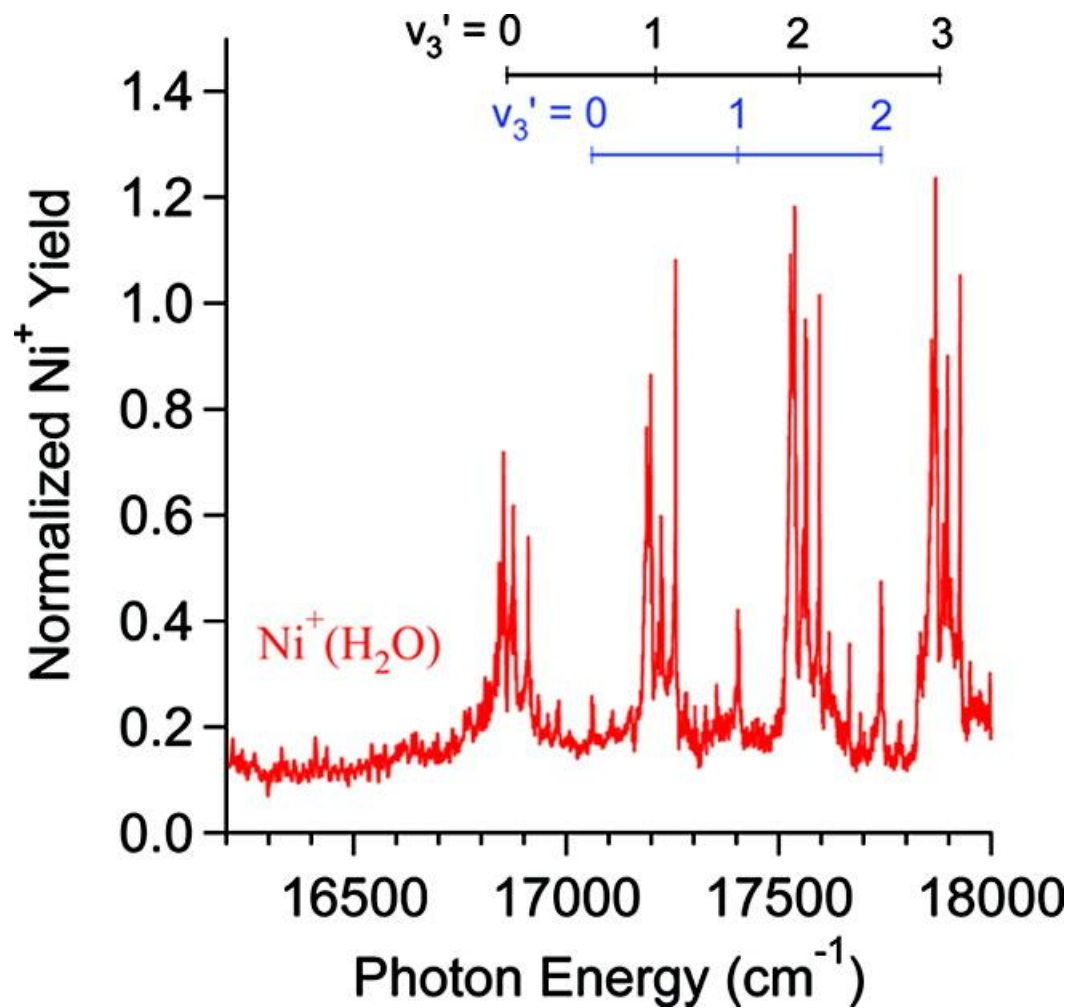


Figure 6.1 $\text{Ni}^+(\text{H}_2\text{O})$ electronic photodissociation spectrum

6.2 Methane Activation by Transition Metals

As extensively discussed in chapters 1, 4, and 5, the activation of methane has been studied for several metal ions and it is worth extending this work to other transition metal ions since they may have very interesting reactivity. Therefore, these studies can be extended in several directions: to other metals, to other intermediates of the C-H activation reaction, and to metal cluster ions. We have studied the complexes using either IRMPD or Ar-tagging. In addition, for complexes with high binding energies, *IR Laser Assisted Photodissociation Spectroscopy*, IRLAPS, or Vibrationally Mediated Photodissociation, VMP, can also be applied. In IRLAPS, a tunable IR excites the molecule as usual; the vibrationally excited molecules are dissociated by absorbing several photons from a high power CO₂ laser.⁴ Our group has applied IRLAPS to measure the vibrational spectrum^{3,4} of Ag⁺(CH₃OH) and VMP to study vibrations of Co⁺(H₂O) (Chapter 3), Ni⁺(H₂O),² and V⁺(OCO).⁵

6.2.1 Second and Third Row Metals

To better understand periodic trends, vibrational spectroscopy of M⁺(CH₄)_n can be extended to several other metals, especially those in the second and third rows. The very next project could be to extend the work presented in Chapter 5 to Au⁺(CH₄)_n. Similarly, Ta, Pd and Pt are good candidates. However, it should be mentioned that studying these metals can be challenging because most third row metals are known to activate methane readily.⁶ In addition, in our experimental setup, the ion source uses metal rods for producing M⁺ ions and some metals are not available or are prohibitively expensive as rods; instead, they are more economical in the form of powder or foil. Our group is currently developing a new source which will allow studying foil or pressed powder samples.

We have attempted to study $\text{Ta}^+(\text{CH}_4)_n$. Unfortunately, Ta^+ readily activates methane, so instead of producing $\text{Ta}^+(\text{CH}_4)$, we produced mostly TaCH_2^+ and several other ions resulting from addition of CH_4 and elimination of H_2 . The reaction cannot be controlled with the current source. But ideally, if the metal ions first react to form $\text{M}^+(\text{Ar})_m$, then this complex reacts with CH_4 to form both Ar-tagged and un-tagged complexes maybe the entrance channel complex can be formed by ligand exchange. Harding *et al.* used this approach to produce $\text{Pt}_x(\text{CH}_4)(\text{Ar})_m$ clusters.⁷ The current source introduces both precursor (CH_4) and bath gases (Ar) to the M^+ that is formed in the laser ablation plasma. Since the CH_4 is present in the hot plasma, it can undergo many different types of reactions, which leads to a very congested mass spectrum. Ideally, we can build a two line source. In the first line, only inert bath gas (Ar, He) is introduced into the ablation region and so only $\text{M}_x^+(\text{Ar})_m$ is produced. Then the precursor (CH_4) can be introduced to react with the cooled $\text{M}_x^+(\text{Ar})_m$. Thus, instead of a direct reaction with M^+ , the CH_4 undergoes a ligand exchange reaction.

6.2.2 Different Intermediates

In the methane activation reaction by transition metal ions (equation 1-1),



there are three major intermediates: entrance channel complex, $\text{M}^+(\text{CH}_4)$, insertion intermediate, $[\text{H-M}^+-\text{CH}_3]$, and exit channel complex, $(\text{H}_2)\text{MCH}_2^+$. Previously our group has studied the MCH_2^+ products for $\text{M}=\text{Fe}, \text{Co}, \text{Ni}$,⁸ Ta ,⁹ and Au .¹⁰

It would be a great extension to study the insertion intermediates of these metals as well. However, we should mention that some of the metals including Co^+ and Ni^+ do not have a stable insertion intermediate and some of the metals like V^+ have insertion intermediates that are local minima but are kinetically un-favored (the barrier between the entrance and insertion

channel complexes is high) and thermodynamically un-favored (the energy of the intermediate is higher than the reactants). All of these considerations should be carefully taken into account. For example, we have calculated that $[\text{H-Ti}^+-\text{CH}_3]$ is thermodynamically favored. Because the barrier between the entrance channel and the intermediate is high, $[\text{H-Ti}^+-\text{CH}_3]$ could be produced by reacting TiCH_2^+ with H_2 . Calculated energies of intermediates of different metals are presented in Table 6-1.

Table 6-1 Relative energies (cm^{-1}) of different intermediates in the C-H activation reaction associated with equation 1-1 at B3LYP/6-311++G(d,p)

M^+	$\text{M}^+ + \text{CH}_4$	$[\text{M}^+(\text{CH}_4)]$	[TS1]	$[\text{HM}^+\text{CH}_3]$
V^+	0	-5166	6160	4235
Ti^+	0	-5457	3887	-527
Fe^+	0			a
Co^+	0	-7692		a
Ni^+	0	-8053		2787

a: Not a local minimum

6.2.3 Metal Cluster Ions

Broader impacts of methane activation by metal ions also involve metal cluster ions since heterogeneous catalysis occurs on metal surfaces, with metallic bonds. Therefore, it would be very interesting to extend the studies of M^+-CH_4 interactions from single metal ions to cluster ions. In addition, the first row metal ions, which do not activate methane at thermal conditions, may activate it when clustered. For example, the barrier to dehydrogenation of methane by Fe_4^+ is substantially lower than for other clusters.¹¹ Thus, in preliminary work, we have studied the interaction between Fe_2^+ and CH_4 ligands via vibrational spectroscopy.

6.2.3.1 Introduction

As discussed in the previous chapters, metals with a $3d^n4s^0$ ground state (such as Co^+ , Ni^+ , and Cu^+) interact more strongly with ligands than those with $3d^{n-1}4s^1$ (such as Mn^+). The Fe^+ ion has a sextet $3d^64s^1$ ground state, but the quartet $3d^7$ is only 1800 cm^{-1} higher in energy. The quartet state binds more strongly to ligands due to the empty $4s$ orbital, so $\text{Fe}^+(\text{CH}_4)$ is a quartet.¹² Combining Fe^+ with neutral, quintet Fe ($3d^64s^2$) leads to many possible spin states for Fe_2^+ . It has been shown that the lowest lying spin states are decaplets, octets and sextets.¹³ Among these, the octet state is calculated as the ground state, but the decaplet lies only $\sim 500\text{ cm}^{-1}$ above it, while the sextet state is much higher in energy. In this preliminary study, we consider only octet states of $\text{Fe}_2^+(\text{CH}_4)_n$.

We have investigated the vibrational spectroscopy of $\text{Fe}_2^+(\text{CH}_4)_n$, for $n=1-2$. Experimental results are compared to calculated spectra of candidate structures to identify the geometry of the complexes.

6.2.3.2 Experimental and Computational Methods

The ions are generated by laser ablation of an iron rod in an expansion gas of pre methane at ~ 15 psi backing pressure. Higher backing pressures produce larger metal clusters. The photodissociation spectrum is obtained by taking the ratio of fragment to parent signal and normalizing to laser power as a function of laser wavelength. For these vibrational spectroscopy studies, a wavelength range of $2500-3100\text{ cm}^{-1}$ was scanned with a Nd:YAG pumped OPO/OPA laser. This produces approximately 5 mJ per pulse near 3000 cm^{-1} , with a line width of 1.8 cm^{-1} .

The calculations were carried out using the B3LYP and CAM-B3LYP hybrid density functional with the 6-311++G(3df,3pd) basis set¹⁴ using the Gaussian 09 program package.¹⁵ Chiodo *et al.* reported that B3LYP is not the best functional for molecules containing metallic

bonds, as it mis-estimates the electronic spin states, and suggested BPW91 instead.¹³ Although we present B3LYP results, other functionals should be evaluated in future work. Calculated binding energies are shown in Table 6-2. For the vibrational spectra of the complexes, the same scaling factor (equation 4-1) derived for Co and Ni is used.

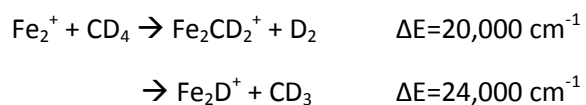
Table 6-2 Calculated binding energies of Fe_2^+ -methane complexes at 6-311++G(3df,3pd) basis set

Molecule	B3LYP	CAM-B3LYP ^a
$\text{Fe}^+ \text{-Fe}$	19763	17360 22100 ^b
$\text{Fe}_2^+ \text{-CH}_4$	3278	4278
$\text{Fe}_2^+ (\text{CH}_4) \text{-CH}_4$	1850	2329
$\text{Fe}_2^+ (\text{CH}_4)_2 \text{-CH}_4$	372	704

^a: The geometry and zero-point energy with B3LYP functional. b: Experimental, from ref.¹⁶

6.2.3.3 Results and Discussion

Difference spectra of $\text{Fe}_2^+(\text{CH}_4)$ and $\text{Fe}_2^+(\text{CH}_4)_2$ are shown in Figure 6.2. The $\text{Fe}_2^+(\text{CH}_4)$ spectrum shows only CH_4 loss while the $\text{Fe}_2^+(\text{CH}_4)_2$ also shows a small amount of 2 CH_4 loss. The GIB study by Liyanage *et al.*¹¹ has shown that the lowest energy products for the reactions of Fe_2^+ with CD_4 are,



The $\text{Fe}_2^+(\text{CH}_4)$ entrance channel complex is calculated to lie $\sim 4000 \text{ cm}^{-1}$ below reactants, so C-H activation via these reactions are $\geq 24000 \text{ cm}^{-1}$ endothermic, so it is not surprising that they are not observed in our IRMPD study.

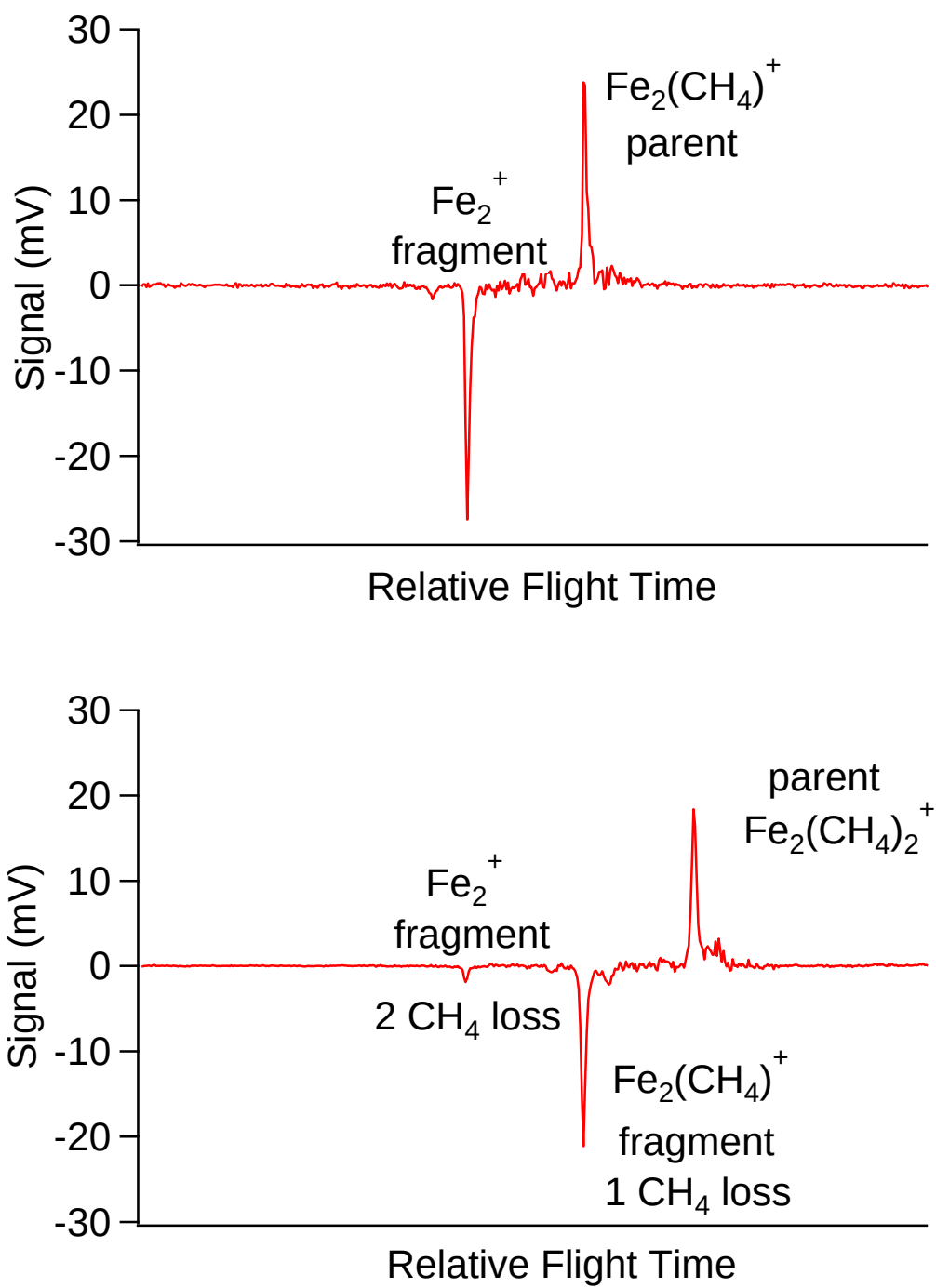


Figure 6.2 Difference spectra of $\text{Fe}_2^+(\text{CH}_4)$ (top) and $\text{Fe}_2^+(\text{CH}_4)_2$ (bottom) at 2804 cm^{-1} and 2828 cm^{-1} , respectively. Both spectra show only methane loss channels, suggesting that the C-H bond is not activated.

6.2.3.4 $\text{Fe}_2^+(\text{CH}_4)$

The binding energy of $\text{Fe}_2^+-\text{CH}_4$ (octet state) is calculated as 4278 cm^{-1} using the CAM-B3LYP functional with 6-311++G(3df,3pd) basis set at B3LYP geometry and zero-point energy. Although this binding energy suggests the photodissociation is not a one photon process, we see relatively high yield ($\sim 10\%$) dissociation by IRMPD.

Figure 6.3 shows the IR photodissociation spectrum of $\text{Fe}_2^+(\text{CH}_4)$, taken by monitoring CH_4 loss. The spectrum consists of a sharp strong doublet at 2804 and 2812 cm^{-1} , with 19 cm^{-1} fwhm, and a very weak feature at 3120 cm^{-1} . The spectrum looks very similar to that of $\text{Mn}^+(\text{CH}_4)$, which has η^3 coordination.¹⁷ The intense peak shows only a small red shift (113 cm^{-1}) from the symmetric stretch in bare CH_4 . This is characteristic of an η^3 structure, and is much smaller than the red shifts we observe for η^2 coordinate $\text{M}^+(\text{CH}_4)$ ($\text{M}=\text{Co}, \text{Ni}, \text{Cu}, \text{Ag}$).

Our calculations predict that the CH_4 binds to one of the irons with coordination between η^2 and η^3 with two Fe-H distances of $2.147\text{ \AA}$ and a Fe-H distance of $2.745\text{ \AA}$. In $\text{Fe}_2^+(\text{CH}_4)$, the HOMO is a Fe-Fe bonding combination of 4s orbitals. The resulting interaction with CH_4 is similar to that in M^+ with $3d^{n-1}4s^1$ occupancy. Thus, the structure and spectrum are similar to those of $\text{Mn}^+(\text{CH}_4)$. The scaled simulated spectrum for this structure is shown in Figure 6.3. As seen from the figure, the simulation predicts the intense vibration at 2719 cm^{-1} , a shift of 100 cm^{-1} from the experiment. This mis-estimate might be for two reasons. First, the scaling factor, which was derived for η^2 coordinate Co and Ni, may not be perfect for this η^3 structure. Thus, it might be over scaled. However, we believe this would bring a shift of not more than 40 cm^{-1} , based on calculations on $\text{Mn}^+(\text{CH}_4)$. The second and more important reason is that the intense vibration is very sensitive to the coordination of methane to Fe^+ , a small shift from η^3 to η^2 shifts the vibration a lot. In the actual case, methane might be in perfect η^3 coordination.

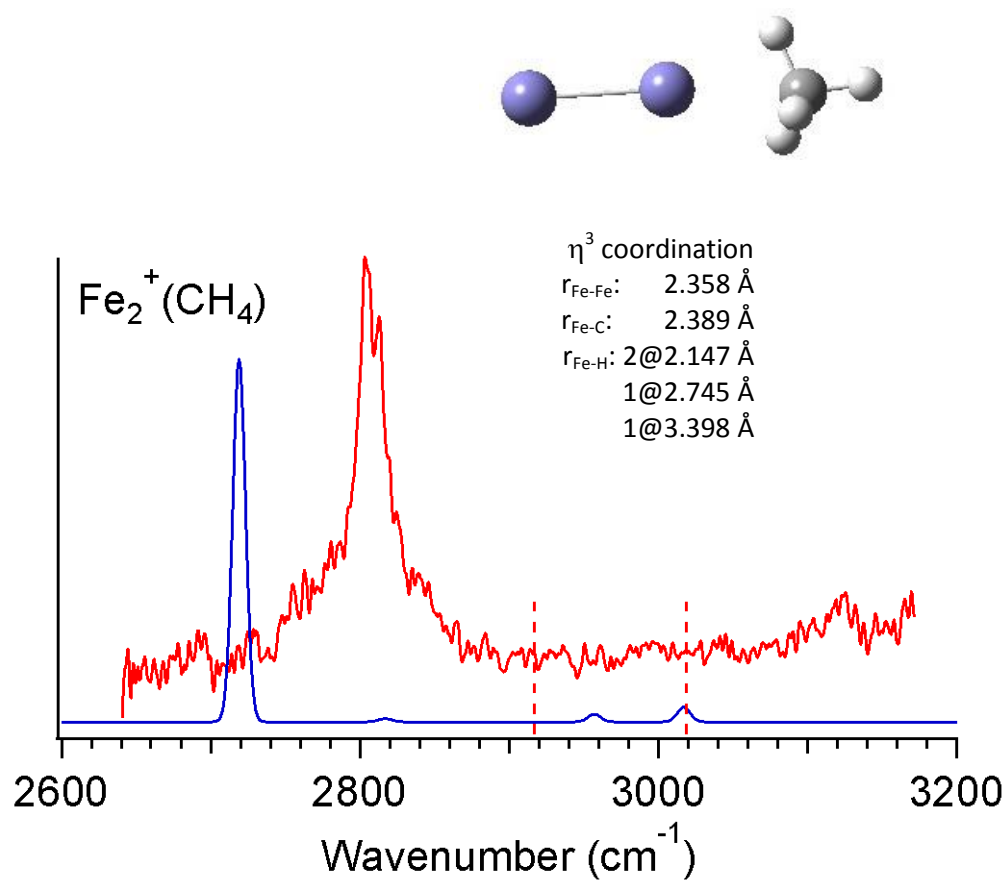


Figure 6.3 IRMPD of $\text{Fe}_2^+(\text{CH}_4)$ complex (red) and calculated simulation (blue) and structure. The solid blue line uses the scaling factor derived by equation 4-1. The vertical dashed lines shows the C-H stretches in bare CH_4 .

Comparing to $\text{Fe}^+(\text{CH}_4)$, which also has η^2 coordination, the observed red shift is smaller in the intense C-H stretch for $\text{Fe}_2^+(\text{CH}_4)$. This can be attributed to delocalization of the charge between the two irons. This leads to a larger metal-ligand distance (Fe-C distance is 2.10 Å in $\text{Fe}^+(\text{CH}_4)$ and 2.389 Å in $\text{Fe}_2^+(\text{CH}_4)$) and weaker interaction, resulting in a substantially smaller red shift. Due to the larger Fe-C distance, the peak due to the distal C-H in the high frequency region is calculated to be very weak and is not observed.

6.2.3.5 $\text{Fe}_2^+(\text{CH}_4)_2$

The binding energy of $\text{Fe}_2^+(\text{CH}_4)\text{-CH}_4$ (octet state) is calculated as 2328 cm^{-1} . This binding energy suggests the photodissociation is a one photon process: we observe high photodissociation yield (~30%).

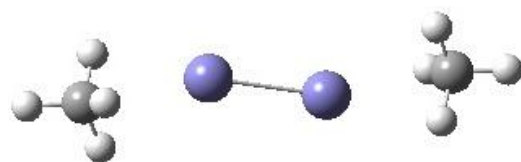
Figure 6.4 shows the IR photodissociation spectrum of $\text{Fe}_2^+(\text{CH}_4)_2$, taken by monitoring CH_4 loss. The spectrum consists of a single strong peak at 2828 cm^{-1} , with 25 cm^{-1} fwhm. This corresponds to the peak in the $\text{Fe}_2^+(\text{CH}_4)$ spectrum, with a slightly smaller red shift from the symmetric stretch in bare CH_4 . The shift from CH_4 is only 89 cm^{-1} . This smaller red shift with increasing number of ligands is consistent with $\text{Mn}^+(\text{CH}_4)_n$.

Our calculations predict that each CH_4 coordinates to one iron in approximately η^3 . The η^3 hydrogens of the two methanes are opposite (gauche) to each other in C_i symmetry. The Fe-C bond distances are 2.462 Å. The mono-metal complexes have the second methane binding to the same metal, so the observed lengthening of the M-C bonds and reduced red shift is to be expected. But in the case of bimetallic complexes, one might think that because the second CH_4 binds to the other Fe, there should not be any change in the first Fe-C distance and thus the spectra of $\text{Fe}_2^+(\text{CH}_4)$ and $\text{Fe}_2^+(\text{CH}_4)_2$ should show the same red shift. We might explain this discrepancy by polarization and charge. In $\text{Fe}_2^+(\text{CH}_4)$, the HOMO is polarized slightly away from

the CH_4 , reducing the repulsion. This polarization cannot occur in $\text{Fe}_2^+(\text{CH}_4)_2$. In addition, in $\text{Fe}_2^+(\text{CH}_4)_2$ there is less total (+) charge on the metals compared to $\text{Fe}_2^+(\text{CH}_4)$, which reduces the electrostatic interaction. The scaled spectrum belonging to this structure is shown in Figure 6.4. The most intense peak is again due to the η^3 hydrogens and is calculated at 2758 cm^{-1} . Again, the calculation predicts a larger red shift than is observed.

These experiments should be carried out on $\text{Fe}_2^+(\text{CH}_4)_n$ ($n>2$) and the calculations should be extended to include other spin states and different functionals which have been found to be more appropriate for metallic clusters.

The vibrational spectroscopy of the Fe_2^+ - methane complexes mirrors the results of GIB reaction studies. The Fe_2^+ is less reactive than Fe^+ .¹¹ Similarly, Fe_2^+ interacts less strongly with methane than Fe^+ . It would be very interesting to extend the spectroscopy to $\text{Fe}_x^+(\text{CH}_4)_n$ ($n>2$). In particular, Fe_4^+ and Fe_5^+ are much more reactive with CH_4 than Fe^+ , due to a lower barrier to formation of the insertion intermediate.^{11,18} In addition, Fe_4^+ has been shown to convert C_2H_4 to benzene.¹⁹



η^3 coordination
 C_i symmetry
 $r_{\text{Fe-Fe}}$: 2.374 Å
 $r_{\text{Fe-C}}$: 2.462 Å
 $r_{\text{Fe-H}}$: 2.191 Å
 2.381 Å
 2.616 Å

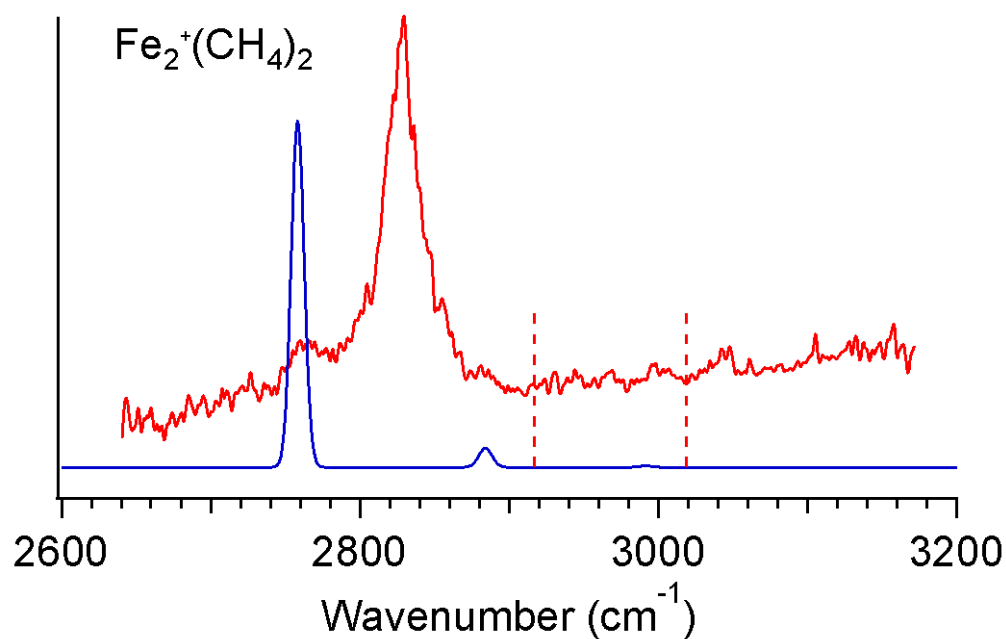


Figure 6.4 IR photodissociation spectrum of $\text{Fe}_2^+(\text{CH}_4)_2$ complex (red), calculated simulation (blue) and structure. The simulation uses the scaling factor derived by equation 4-1. The vertical dashed lines shows the C-H stretches in bare CH_4 .

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