REVIEW

Infrared Spectra, Structures and Bonding of Binuclear Transition Metal Carbonyl Cluster Ions

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Binuclear transition metal carbonyl clusters serve as the simplest models in understanding metal-metal and ligand bonding that are important organometallic chemistry catalysis. Binuclear first row transition metal carbonyl ions are produced via a pulsed laser vaporization/supersonic expansion cluster ion source in the gas phase. These ions are studied by mass-selected infrared photodissociation spectroscopy in the carbonyl stretching frequency region. Density functional theory calculations have been performed on the geometric structures and vibrational spectra of the carbonyl ions. Their geometric and electronic structures are determined by comparison of the experimental IR spectra with the simulated spectra.

The structure and the metal-metal and metal-CO bonding of both saturated and unsaturated homonuclear as well as heteronuclear carbonyl cluster cations and anions are discussed.

Key words: Transition metal carbonyl complex, Infrared photodissociation spectroscopy, Metal-metal bonding, Metal-ligand interaction, The 18-electron rule

I. INTRODUCTION

Since the first synthesis of heteroleptic metal carbonyl complex Pt(CO)$_2$Cl$_2$ and homoleptic complexes Ni(CO)$_4$ and Fe(CO)$_5$, the metal carbonyl chemistry has evolved to be a long-standing attractive field in organometallic chemistry. A large number of transition metal carbonyl complexes and their derivatives have been synthesized, which are not only of close relevance to many industrial processes in synthesis [1] and catalysis [2] but also frequently regarded as prototypical models in understanding the fundamental concepts of chemistry, such as the metal-ligand and metal-metal bonding as well as the effectiveness of the electron counting rule (18-electron rule) [3–6].

Neutral transition metal carbonyl compounds that are stable at ambient conditions are most commonly encountered. Mononuclear carbonyls including Ni(CO)$_4$, Fe(CO)$_5$, and Cr(CO)$_6$, as well as multinuclear carbonyl clusters such as Mn$_2$(CO)$_{10}$, Fe$_2$(CO)$_9$, Fe$_3$(CO)$_{12}$, and Co$_4$(CO)$_{12}$ are well-known stable homoleptic carbonyls, which are widely used as starting materials in synthetic transition-metal organometallic chemistry [7]. In addition, a variety of charged metal carbonyls have also been synthesized in the condensed phase, isolated as salts with appropriate counter ions [8, 9]. These stable carbonyl compounds are in general saturate-coordinated and obey the 18-electron rule.

Besides the stable saturate-coordinated carbonyl compounds, coordinatively unsaturated transition-metal carbonyls have received particular attention [10]. These species are often building blocks of stable organometallic complexes and engage in a wide variety of chemical processes as reaction intermediates and can be exceedingly reactive. Spectroscopic characterization of these highly active unsaturated metal carbonyls is crucial in understanding the intrinsic reaction mechanism involving carbonyl compounds or carbon monoxide. Binary unsaturated transition metal carbonyls across the period table have been produced and isolated in low-temperature noble gas matrices and studied spectroscopically [10]. Much of what is known about the unsaturated mononuclear transition metal carbonyls comes from matrix-isolation infrared absorption spectroscopic studies. With advances in light sources, time-resolved absorption spectroscopy has been applied to investigate coordinatively unsaturated metal carbonyl neutrals in the gas phase [11, 12]. Compared with matrix-isolation spectroscopic studies, gas-phase studies provide not only spectroscopic information but also reaction kinetics and photophysical properties of unsaturated transition-metal carbonyl species.

Saturated and unsaturated metal carbonyl ions can also be produced in the gas phase, which have been studied extensively by mass spectrometry that provides thermochemical and photochemical properties [13]. Gas-phase spectroscopic studies have also been performed to

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gain detailed vibrational and structural information of carbonyl ions. Photoelectron spectroscopy is quite widely used for mass-selected metal carbonyl anions [14−25]. Infrared photodissociation spectroscopy offers one of the most direct and generally applicable experimental approaches to obtain vibrational spectra of mass-selected ions in the gas phase [26−30]. This technique has been successfully employed in studying multinuclear transition metal cluster carbonyls with infrared free electron lasers [31−36]. Mononuclear metal carbonyl cation complexes have also been studied with mass-selected infrared photodissociation spectroscopy with the OPA/OPO laser system [37−45], among which selected results have been reviewed by Duncan [46]. Recently, we have investigated the vibrational spectra of various transition metal carbonyl ions produced in the gas phase using infrared photodissociation spectroscopy [47−59]. In this paper, we provide a review of these results, in particular, we will focus on the structure and bonding of the binuclear first row transition metal carbonyl ions.

II. EXPERIMENTS

The details of the experiments have been described in previous publications [60, 61]. The transition metal carbonyl ions are prepared in a Smalley-type laser vaporization supersonic expansion ion source using the 1064 nm fundamental of a Nd:YAG laser (Continuum, Minilite II, 10 Hz repetition rate and 6 ns pulse width). The laser is focused onto a rotating and translating metal target. The expansion gas is helium seeded with 2%−10% CO at a backing pressure of 0.4−1.0 MPa. Heteronuclear cluster ions are produced using a uniformly mixed metal target, which was prepared by pressing mixtures of metal powders. The ions undergo a supersonic expansion to form a collimated and cold molecular beam, and are pulse-extracted into a time-of-flight mass spectrometer.

Ions of specific mass are selected by their flight time with a mass gate and decelerated into the extraction region of a second collinear time-of-flight mass spectrometer, where they are subjected to infrared photodissociation. The tunable IR laser beam is generated by a KTP/KTA/AgGaSe2 optical parametric oscillator/amplifier system (OPO/OPA, Laser Vision) pumped by a Continuum Powerlite 8000 Nd:YAG laser. When the IR laser is on resonance with the vibrational fundamental of the ion complex, single or multiple photon absorption can take place, leading to the dissociation of the complex. The fragment ions together with the undissociated parent ions are reaccelerated and detected by the second time-of-flight mass spectrometer. IR spectra are recorded by monitoring the relative yield of fragment ions as a function of the photodissociation IR laser wavelength. Spectra are recorded typically by scanning the dissociation laser at step of 2 cm−1 and averaging over 250−400 laser shots at each wavelength.

Quantum chemical calculations have been performed to determine the molecular structures and to support the assignment of vibrational spectra of the studied metal carbonyl cluster ions. Details of these calculations can be found in the original papers [47−59]. In general, geometry optimization and harmonic vibrational frequency analysis are performed with the most popular hybrid B3LYP density functional theory [62, 63], which has been shown to be able to provide reliable predictions on the structures and vibrational frequencies of transition metal-containing compounds [64, 65]. Other functionals have also been used for selected systems. Different basis sets are employed for different systems, as described in the original papers. For the unsaturated carbonyl clusters, all possible spin states are considered. The calculated harmonic vibrational frequencies are scaled to correct for the anharmonic effect to compare with the experimental vibrational frequencies [66]. All calculations are performed using the Gaussian 09 suite of quantum chemical software packages [67].

III. RESULTS AND DISCUSSION

A. The mass spectra

The mass spectrum depends strongly on the conditions of the ion source, including the vaporization laser power, carrier gas stagnation pressures, and in particular, the timing between the vaporization laser and the supersonic expansion. FIG. 1 shows the mass spectra of the nickel carbonyl cation complexes produced by pulsed laser vaporization of a nickel metal target in an expansion of helium seeded by carbon monoxide at different experimental conditions. Spectrum (a) is obtained from experiment with short time delay between pulsed valve and vaporization laser. This spectrum demonstrates the production of mononuclear nickel carbonyl cation complexes containing up to 8 CO’s. These cluster ions contain both strongly bound ligands coordinated to metal and weakly bound ligands attached to the external surface of stable complexes, which are formed only because of the cold supersonic beam conditions. Spectrum (b) is obtained from experiment with long time delay between pulsed valve and vaporization laser. At this experimental condition, only those ions with relatively strong bonding can survive. The mass spectrum is dominated by the signals of saturated or near saturate coordinated nickel cluster carbonyls corresponding to Ni(CO)5+, Ni2(CO)8+, and Ni3(CO)9+. The observed spectral features provide valuable information on the maximum number of CO molecules (saturation limits) that bind to small nickel cluster cations. The Ni+ cation has a surprising high coordination number of five toward CO. The Ni(CO)5+ cation is characterized to be a fivefold coordinated trigonal bipyrami-
dial carbonyl complex having 19 valence electrons with the extra electron residing largely on metal center [47]. The Ni$_2^{2+}$ cation is determined to have a coordination number limit of eight based on the mass spectrum. The Ni$_3$(CO)$_9^{2+}$ cluster cation is the only trinuclear carbonyl species observed in the mass spectrum, suggesting that the saturation limit of CO coordination on Ni$_3^{2+}$ is nine, in agreement with previous reports [68]. The saturation limit of Ni$_4^{2+}$ is determined to be 11 instead of previously reported 10 [68].

Although the metal-metal and metal-CO bond energies of the binuclear metal carbonyl ions are in general much greater than the energy of IR photons in the CO stretching frequency region, photodissociation by losing one or more CO ligands can still be observed. The signal detected is likely due to multiple photon absorption, which is not expected to be very efficient at the low laser pulse energies used here (about 1 mJ/pulse), but can be detected due to high IR oscillator strength of the carbonyl stretching vibrations. Ion complexes containing weakly bound CO ligands can also be formed under cold supersonic beam conditions. For such CO-tagging complexes, elimination of the tagged CO is a very efficient one-photon process. Besides the fragmentation channel via loss of CO, other dissociation channels are also observed in some cluster cations, which provide very valuable information about the geometric structure of the cations. For instance, the fragmentation channel via the loss of a copper atom is observed for the CuFe(CO)$_4^{−}$ cluster anion [56], which implies that it has a Cu-Fe(CO)$_4$ structure with all the four CO ligands coordinated on the Fe center. The Ni$_2$(CO)$_8^{2+}$ cation dissociates quite efficiently via loss of a Ni(CO)$_4$ fragment with low laser energy [54]. This observation suggests that the Ni$_2$(CO)$_8^{2+}$ cluster cation has a symmetric (OC)$_4$Ni-Ni(CO)$_4$ structure with a weak Ni–Ni bond. The absence of the CO fragmentation channel indicates that the Ni–Ni bond is weaker than the Ni–CO bond.

**B. CO binding modes and the carbonyl stretching frequencies**

The carbon monoxide ligand binds terminally to the metal center in mononuclear metal carbonyl complexes, but engages in a range of bonding modes in bi- and multinuclear carbonyl clusters. The various possible binding modes of CO in binuclear metal carbonyl clusters are summarized in FIG. 2. Besides the ubiquitous terminal end-on type (a), the other well-known coordination modes are the end-on bridging types having either symmetrical (type b) or unsymmetrical (semi-bridging type c) structures. Bridging carbonyl ligands that are bonded via both carbon and oxygen atoms to metal atoms are also possible, which can formally be classified into two types, namely the side-on bridging type (d) and type (e) with a linear M-C-O-M linkage.

Infrared spectroscopy is the most widely used analytical technique for the characterization of metal carbonyls. Transition-metal carbonyls exhibit strong absorptions in the C-O stretching vibrational frequency region. The CO stretching vibrational frequency correlates with the strength of carbon-oxygen bond, which is a direct consequence of the bonding interactions between metal and CO. The bonding interactions between carbon monoxide and the metal center can be described using the Dewar-Chatt-Duncanson model [69, 70], which involves synergic $σ$ donation from the carbon lone-pair $5σ$ orbital to the metal and $π$ back-donation of electron density from the transition metal $d$ orbitals into the $2π^*$ antibonding orbitals of CO. The $π$ back-donation tends to weaken the CO bond and causes a red-shift of the CO stretching frequency. The $σ$ donation has a much weaker impact on the carbonyl stretching frequency than $π$ back-donation, as the $5σ$ orbital of CO is largely nonbonding in character. When CO is coordinated to a positively charged metal center, the carbonyl complex exhibits very little metal to CO $π$ back-
donation and the bonding interactions come mainly from CO to metal σ donation [71–73]. Such carbonyl complexes have been termed as nonclassical carbonyls that possess blue-shifted CO stretching frequencies [74, 75]. The electrostatic interaction is the driving force to lead to a blue-shift of the carbonyl stretching frequencies [76–78].

Among the homoleptic binuclear first row transition metal carbonyl cation complexes studied, the Fe₂(CO)₉⁺, Fe₂(CO)₇⁺ [48], Ni₂(CO)₇⁺, Ni₂(CO)₉⁺ [54], and Cu₂(CO)₉⁺ [53] cation complexes are determined to involve only the terminal end-on type CO ligands. Heteronuclear cations including FeM(CO)₅⁺ (M=Co, Ni and Cu), MCu(CO)₇⁺ (M=Co and Ni) [57], FeZn(CO)₅⁺ and CoZn(CO)₇⁺ [58] are characterized to be terminally bonded as well. The IR active carbonyl stretching modes are observed in the range of 2030–2220 cm⁻¹, either blue-shifted or slightly red-shifted from that of free CO at 2143 cm⁻¹, suggesting weak metal to CO π back donation bonding in these carbonyl cation complexes. Binuclear anion complexes including homoleptic Fe₂(CO)₉⁻ (n=4–8) [49] and heteronuclear FeCu(CO)₇⁻ (n=4–7) [56] are also studied, which are elucidated to have metal-metal bonded structures with all of the carbonyl ligands terminally bonded as well. The CO stretching frequencies are observed in the range of 1800–2100 cm⁻¹, which are red-shifted from that of free CO.

The Co₂(CO)₉⁺ cation complex is the only binuclear species among the studied later first row transition metal systems that involves an end-on bridging carbonyl ligand [55]. The infrared photodissociation spectrum is shown in FIG. 3, along with the optimized structure. The spectrum exhibits three bands centered at 1941, 2068, and 2131 cm⁻¹, indicating the cation complex involves end-on bridge-bonded carbonyl ligands(s). The cation is determined to have Cs symmetry involving a bridging CO ligand. At the B3LYP/6-311+G* level, the two Co–C bond distances to the bridging CO ligand are predicted to be 1.861 and 2.233 Å, respectively, indicating a semibridging type of bonding. The bond length of the bridging CO ligand of 1.157 Å is longer than those of the terminal bonded ligands (1.136–1.141 Å).

The infrared spectrum of Ti₂(CO)₇⁺ is illustrated in FIG. 4 [52]. The spectrum exhibits six partially resolved bands in the 2100–2200 cm⁻¹ region, which can be attributed to the terminal carbonyl stretching vibrations. Three additional bands centered at 1942, 1655, and 1685 cm⁻¹ are observed in the low frequency region. The 1942 cm⁻¹ band is originated from a semibridging CO ligand. The much low CO stretching frequencies at 1655 and 1685 cm⁻¹ are attributed to the antisymmetric and symmetric stretching vibrations of two side-on bridging carbonyl ligands. The cation is predicted to have Cs symmetry involving a semibridging carbonyl ligand and two equivalent side-on bridging carbonyl ligands (FIG. 4). The two side-on bridging carbonyls are predicted to have a quite long C–O bond distance of 1.181 Å at the B3LYP/6-311+G* level. The semibridging CO distance of 1.144 Å is 0.037 Å shorter than that of the side-on bridging groups but is about 0.02 Å longer than those of the terminal CO ligands.

The bonding molecular orbitals related to the side-on bridging carbonyl ligands in Ti₂(CO)₇⁺ are shown in FIG. 5. The side-on bridging carbonyl groups act as both the usual type of σ donor to the left-hand titanium atom (HOMO-6 and HOMO-7) and π donor to the right-hand titanium center through the C=O π bonds (HOMO-14 and HOMO-16). Thereby, each side-on bridging CO ligand serves as a four-electron donor. Similar four-electron donor side-on bridging carbonyl ligands have previously been observed in a few organometallic complexes [79–81] and in the neutral homoleptic Sc₂CO, Ti₂(CO)₂ and Lu₂(CO)₂ (x=1, 2) complexes [82–86].

The Cr₂(CO)₉⁺ (n=7–9) cation complexes are unique among the homoleptic binuclear first row transition metal carbonyl cation complexes. All of the three Cr₂(CO)₉⁺ cation complexes are determined to have the (OC)₅Cr–C–O–Cr(OC)₅⁺ structures each involving a linear bridging carbonyl group bonded to...
one chromium atom through its carbon atom and to the other chromium atom through its oxygen atom [51]. The infrared spectrum of \(\text{Cr}_2(\text{CO})_9^+\) is shown in FIG. 5, which exhibits six well-resolved bands at 1797, 2036, 2094, 2134, 2154 and 2174 cm\(^{-1}\). The later five bands above 2000 cm\(^{-1}\) are attributed to the terminal carbonyls. The 1797 cm\(^{-1}\) band is due to the stretching vibration of the linear bridging carbonyl group. The \(\text{Cr}_2(\text{CO})_9^+\) cation has a sextet ground state with \(C_s\) symmetry (FIG. 6). The bridging CO ligand is predicted to have a bond distance of 1.182 Å at the B3LYP/6-31+G* level. The linear bridging carbonyl bonding mode is quite uncommon. It was previously found in binuclear metal carbonyl derivatives, including the experimentally known \((\eta^5-\text{Me}_5\text{C}_5)_2\text{V}=\text{O}–\text{C}–\text{V}(\text{CO})_5\) [87].

The bonding molecular orbitals related to the linear bridging CO of \(\text{Cr}_2(\text{CO})_7^+\) are shown in FIG. 7. The \(\text{Cr}–\text{CO}\) interactions in the linear bridging CO can be described by the popular Dewar-Chatt-Duncanson model involving both the CO 5σ to metal donation (HOMO-15) and the metal to CO 2π* back-donation (HOMO-1, doubly degenerate). Similar bonding is observed in the Cr–OC interactions in which the metal is bonded to the oxygen atom of the CO group rather than the carbon atom. The σ bond is formed via the overlap of the LUMO orbital of \(\text{CrCO}^+\) with the CO 4σ orbital (HOMO-27). The back-donation π bonds are formed through overlap of the perpendicular pair of π orbitals of the \(\text{CrCO}^+\) fragment with the 2π* antibonding orbitals of the CO ligand (HOMO-5, doubly degenerate). In this regard, the linear bridging CO ligand serves as a four electron donor.

C. The 18-electron rule

The simple 18-electron rule is often successful in interpreting the structure and metal-metal and metal-CO bonding of stable transition metal carbonyl compounds. The unsaturated binuclear carbonyl ion complexes have no enough valence electrons to satisfy the 18-electron

FIG. 5 Bonding molecular orbitals related to the side-on bridging CO ligands in \(\text{Ti}_2(\text{CO})_9^+\).

FIG. 6 Infrared photodissociation spectrum and optimized structure of \(\text{Cr}_2(\text{CO})_9^+\).

FIG. 7 The bonding orbitals related to the linear bridging CO ligand in \(\text{Cr}_2(\text{CO})_7^+\).
configuration of both metal centers. In this circumstance, it is found that the binuclear metal carbonyl ions adopt asymmetric structures to satisfy the 18-electron configuration of one metal center. In this regard, the neutral Ni(CO)$_4$, Fe(CO)$_5$ and Cr(CO)$_6$ fragments are found to be building blocks in both the homonuclear and heteronuclear cation complexes [48, 51, 54, 57, 58].

The Cr$_2$(CO)$_n^+$ cluster cations all are characterized to have sextet ground states with (OC)$_5$Cr−C−O−Cr(CO)$_n$−6$^+$ structures that can be regarded as being formed via the interaction between a Cr(CO)$_6$ neutral fragment and a Cr(CO)$_n$−6$^+$ cation fragment [51]. Molecular orbital analysis and spin population analysis indicate that the charge and unpaired electrons all are located on the Cr(CO)$_n$−6 moiety. The chromium center in the Cr(CO)$_6$ subunit has 18 formal valence electron configuration, while the other chromium center has only 9, 11, and 13 valence electrons for the $n$=7, 8, and 9 complexes, respectively.

Both the homonuclear Fe$_2$(CO)$_8^+$ and Fe$_2$(CO)$_9^+$ cations have asymmetric (OC)$_5$Fe-Fe(CO)$_3$4$^+$ structures involving a common square pyramid like Fe(CO)$_5$ group (FIG. 8). The iron center in the Fe(CO)$_5$ subunit has 18 formal valence electron configuration, while the other iron center has only 15 or 17 valence electrons. The experimentally observed heteronuclear FeM'(CO)$_8^+$ (M'=Co, Ni, Cu) complexes are determined to have eclipsed (CO)$_5$Fe-M(CO)$_3$ structures each involving a square pyramid Fe(CO)$_5$ subunit with C$_4v$ symmetry [57]. Natural population analysis indicates that the charge and spin are largely located on the M(CO)$_3$ subunit. Therefore, these complexes can be viewed as interaction between a neutral Fe(CO)$_5$ fragment and a M(CO)$_3$+ (M=Co, Ni, Cu) fragment. The 18-electron Fe(CO)$_5$ neutral serves as a two-electron donor in these cation complexes, with the Co, Ni and Cu centers having 16, 17 and 18 valence electrons, respectively.

Similar bonding situation is observed in both the homonuclear and heteronuclear carbonyl anion complexes. The experimentally observed CuFe(CO)$_n^−$ ($n$=4−7) cluster anions are characterized to have Fe-Cu bonded (OC)$_4$Fe-Cu(CO)$_n$−4 structures (FIG. 9), each involving a C$_3v$ symmetry Fe(CO)$_4$− building block with an 18-electron configuration iron center [56]. The preference to form the Fe(CO)$_4$− building block in the CuFe(CO)$_n$− ($n$=4−7) cluster anions is easy to understand. The Fe(CO)$_n$− anions were experimentally determined to have quite large metal carbonyl bond dissociation energies (FeCO$^-$: (33.7±3.5) kcal/mol, Fe(CO)$_2^-$: (35.7±3.5) kcal/mol, Fe(CO)$_3^-$: (42.4±3.5) kcal/mol, Fe(CO)$_4^-$: (41.7±2.5) kcal/mol) [89], which are significantly larger than those calculated values of copper carbonyl anions (CuCO$^-$: 3.2 kcal/mol, Cu(CO)$_2^-$: 13.0 kcal/mol, Cu(CO)$_3^-$: 29.4 kcal/mol). Recent photoelectron velocity-map imaging experiments in conjunction with theoretical calculations of CuNi(CO)$_n$− ($n$=2−4) indicate that the carbonyl groups are preferentially bonded to the nickel atom [22]. When the nickel center satisfies the 18-electron configuration, the copper atom starts to adsorb additional CO molecules. The homonuclear Fe$_2$(CO)$_n^−$ complexes are found to be building blocks in both the homonuclear and heteronuclear cation complexes [48, 51, 54, 57, 58].

![FIG. 8 Optimized structures of the Fe$_2$(CO)$_n^+$, Fe$_2$(CO)$_n^−$, and Fe$_2$(CO)$_n^−$ (n=8, 9).](image1)

![FIG. 9 Optimized structures of the CuFe(CO)$_n^−$ (n=4−7) anions.](image2)
(n=4−7) cluster anions are characterized to have similar asymmetric (OC)4Fe-Fe(CO)n−4 structures as well [49]. Natural bond orbital analysis shows that the negative charge is mainly located on the Fe(CO)4 moiety, while the unpaired electrons all are located on the Fe(CO)n−4 moiety. The cluster anions can be regarded as being formed via the interaction between a Fe(CO)4− anion and a Fe(CO)n−4 neutral fragment in forming a Fe−Fe single bond to satisfy the 18-electron configuration of the tetra-carbonyl coordinated iron center. The preference for asymmetric structures in these homonuclear cluster anions is also due to different metal-carbonyl bond strengths. The metal carbonyl bond strengths of Fe(CO)4− (41.7±2.5 kcal/mol) and Fe(CO)3− (42.4±3.5 kcal/mol) are larger than those of FeCO− (33.7±3.5 kcal/mol) and Fe(CO)2− (35.7±3.5 kcal/mol) [89].

D. Metal-metal bonding

Metal-metal bonding is an extremely important issue in transition metal chemistry. All of the binuclear first row transition metal carbonyl ion complexes in the present study have metal-metal bonded structures except the Cr2(CO)6+ (n=7−9) cation complexes, which possess a linear Cr−C−O−Cr structural motif without a chromium-chromium bond. The preference of the structures without Cr−Cr bonding can be rationalized in terms of different bond strength between the Cr−Cr and Cr−CO bonds [51]. Chromium is known to form weak Cr−Cr bonds. The dissociation energy of Cr2 (1Σ2+) with a formal bond order of 6 is reported to be only 1.443−1.53 eV [90]. In contrast, chromium is able to form strong bonds with CO. The dissociation energy of the first CO in Cr(CO)6 was determined to be (36.8±2) kcal/mol [91].

The other coordination saturated and unsaturated binuclear first row transition metal carbonyl ion complexes studied are either metal-metal single or half bonded. Although metal-metal multiple bonding has been theoretically predicted to be available in some unsaturated homoleptic binuclear carbonyl neutrals [92, 93], no metal-metal multiple bonds exist in the binuclear first row transition metal carbonyl ion complexes studied. The preference of the asymmetric structures involving saturate coordinated 18-electron building blocks precludes the incorporating of metal-metal multiple bonds in these complexes. In the binuclear cation complexes including Fe2(CO)8+, Fe2(CO)9+, Ni2(CO)8+, and (OC)3Fe-M(CO)4+ (M=Co, Ni, Cu), which involve an 18-electron neutral fragment and an unsaturated cation fragment, the metal-metal bonds are characterized to be an σ-type neutral fragment→cation fragment dative single bond. If both fragments are unsaturated, the metal-metal bond is better regarded as an electron sharing single bond, as demonstrated in the (CO)4Co-Zn(CO)3+ cation complex as well as the (OC)4Fe-Fe(CO)4− (n=4−8) and (OC)4Fe-Cu(CO)n−4 (n=4−7) anion complexes [49, 56, 58].

The Ni2(CO)8+ and Cu2(CO)6+ cation complexes are the only two exceptions that adopt symmetric geometric structures (FIG. 10). The Ni2(CO)8+ complex has D3d symmetry involving two equivalent C3v symmetric Ni(CO)4 subunits [54]. The Ni−Ni bond is characterized to be one electron-sharing half bond with both nickel centers exhibiting the favored 18-electron configuration. The Cu2(CO)6+ cation has a staggered D3d structure with three terminally bonded carbonyls on each copper center. The Cu−Cu bond is also a half bond with both copper centers exhibiting 17 valence electrons [53].

Metal-metal multiple bonding is found to exist in ultra-unsaturated heteronuclear carbonyl anion complexes. Recent study [59] on the UFe(CO)3− and OUFe(CO)3− anion complexes indicates that both anions have C3v symmetry with all the carbonyl ligands bonded on Fe center (FIG. 11). Bonding analyses indicate that UFe(CO)3− can be regarded as being formed via interactions between the U atom in quintet spin state with (5f)6(6d)1(7s)2 configuration and the Fe(CO)3− fragment in the 2A1 spin state in forming one electron-sharing σ bond and two Fe-to-U dative π bonds. The formal oxidation states of uranium and iron can be assigned as U(I) and Fe(-II). The OUFe(CO)3− anion has quite similar bonding situation. The anion can be regarded as being formed between a triplet excited state of UO fragment with U(5f)2(7s)2 configuration and the Fe(CO)3− fragment in forming one covalent σ bond two Fe-to-U dative π bonds. The formal oxidation states of uranium and iron are U(III) and Fe(-II).

E. The effect of charge

The present experiments provide detailed vibrational spectra and structures on charged carbonyl clusters in the gas phase for comparison to the neutral species previously known in understanding the charge effect. Iron carbonyls provide a good example for such comparison. Both the cations and anions with chemical formula of Fe2(CO)9 and Fe2(CO)9 are studied in the present experiments [48, 49]. The Fe2(CO)9 neutral is a well-known stable iron carbonyl, which has a tribridged structure with D3h symmetry [94]. This structure is not a local minimum for the Fe2(CO)9+ cation (FIG. 8). Theoretical calculations starting with this initial structure without symmetry constraint, the optimization ended up with the lowest-energy structure having a (OC)3Fe−Fe(CO)4+ geometry with all of the carbonyl ligands terminally bonded. The Fe2(CO)9− anion is a weakly bound complex involving a Fe2(CO)9− core anion that is solvated by an external CO molecule. The Fe2(CO)8− anion is determined to have an unbridged C3 structure with all of the carbonyl ligands terminally bonded.

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FIG. 10 Optimized structures of Ni$_2$(CO)$_8^+$ and Cu$_2$(CO)$_6^+$.

FIG. 11 Optimized structures of UFe(CO)$_3^-$ and OUFe(CO)$_3^+$.  

bonded (FIG. 8). The Fe$_2$(CO)$_8^-$ neutral was determined to have two structures. One is a dibridged structure (FIG. 8), which was predicted to be the lowest energy structure of Fe$_2$(CO)$_8$ [95]. The second high energy structure was deduced to be an unbridged structure, and its infrared spectrum is consistent with the D$_{2h}$ geometry predicted from theory [96]. The Fe$_2$(CO)$_8^+$ cation is determined to have an unbridged asymmetric (OC)$_5$Fe-Fe(CO)$_3^+$ structure. The results imply that both the cations and anions prefer unbridged structures, whereas the neutrals prefer bridged structures.

The only observation of the unbridged structure of Fe$_2$(CO)$_8^-$ seems to contradict the previous experiment using the FTICR apparatus with an infrared free electron laser, in which the experimentally observed Fe$_2$(CO)$_8^-$ anion was characterized to have a C$_s$ structure involving two bridge-bonded CO ligands absorbing at around 1770 cm$^{-1}$[33]. These two structures are computed to be quite close in energy with the unbridged structure being slightly lower in energy. As Moore et al. pointed out [33], although the calculation for the dibridged structure agrees with the experiment, the unbridged structure also agrees well in the terminal CO region, and thus the coexistence of both structures cannot be excluded. The Fe$_2$(CO)$_8^-$ anion was produced via ion-molecular reactions in the previous FTICR experiment [33], and the ions may be thermalized by collisions. Therefore, both structures can be populated. In the present experiment, the supersonic expansion conditions make very cold ions, and only the lowest energy structure would survive to be studied.

Similar structural change from bridging in neutral to terminal CO in ions is also observed in the cobalt carbonyl system. The Co$_2$(CO)$_8$ neutral is the simplest stable closed-shell cobalt carbonyl, which is commercially available and has the well-known dibridged crystal structure of C$_{2v}$ symmetry [97]. The Co$_2$(CO)$_8^+$ cation involves only one semi-bridging CO ligand. As has been discussed [98], the HOMO of the neutral complexes that involves bridging carbonyl ligands is bonding in character with respect to the metal-CO bridging bonds. Upon removing one electron from HOMO, the electron density between the metal atoms and the bridging CO ligands is reduced, leading to the destabilization of the bridged structures.

The binuclear titanium carbonyl cation system provides another example for exploring the charge effect. Early transition metals with fewer valence electrons than later transition metals, needs to bind more ligands to accomplish the 18-electrons configuration. But saturated coordination usually causes steric repulsion between ligands. In this regard, the 18-electron rule is less strict for early transition metals. The stable configuration is a compromise between the inclination of 18-electrons and the steric repulsion of ligands. In the study of binuclear titanium carbonyl cations, a Ti$_2$(CO)$_9^+$ cation is also formed along with the Ti$_2$(CO)$_9^+$ cation, both are observed to be the most intense peaks in the mass spectrum. As mentioned above, the Ti$_2$(CO)$_9^+$ cluster cation has an equilibrium structure with two equivalent side-on bridging carbonyls and one semibridging carbonyl. In contrast, the Ti$_2$(CO)$_9^+$ cation with more oxophilic titanium centers involves only one side-on bridging carbonyl ligands (FIG. 4). The two titanium centers have 17 and 14 electrons in Ti$_2$(CO)$_9^+$, and 16 and 15 electrons in Ti$_2$(CO)$_9^+$.

**IV. CONCLUSION**

The method of pulsed laser vaporization/supersonic expansion is very powerful in preparing a variety of binuclear transition metal carbonyl ions in the gas
phase for mass-selected infrared photodissociation spectroscopy study. The present experiments allow us to investigate the unsaturated and saturated homonuclear and heteronuclear carbonyl ions. The high IR oscillator strength of the carbonyl stretching vibrations makes it possible to obtain the infrared spectra of the chemically bound carbonyl cluster ions in the carbonyl stretching frequency region via multiphoton absorption.

These infrared photodissociation experiments provide clear determination of the carbonyl bonding on the transition metal dimer cations. A range of bonding modes are observed. Besides the ubiquitous terminal end-on bonding mode, which is observed in all of the binuclear cluster ions studied, the end-on semibridging bonding mode is also shown to exist in both early and later transition metal cation complexes. Bridging carbonyl ligands that are bonded via both carbon and oxygen atoms to the metal centers are also observed in early transition metal cluster ions, including the side-on bridging and the linear bridging modes, both of which serve as four-electron donor ligands. Most of the studied later transition metal binuclear ion complexes are characterized to have unbridged structures with all of the carbonyl ligands terminally bonded.

Unlike the well-known neutral clusters such as Fe₂(CO)₉, Fe₂(CO)₉ and CO₂(CO)₈, which have symmetric structures with both metal centers being equally coordinated, the unsaturated binuclear metal carbonyl ions adopt asymmetric structures to satisfy the 18-electron configuration of one metal center. The neutral Ni(CO)₄, Fe(CO)₅ and Cr(CO)₆ fragments and the Fe(CO)₄⁻ anion are found to serve as common building blocks in these homonuclear as well as heteronuclear ion complexes.

The preference of the asymmetric structures involving saturate coordinated building blocks precludes the incorporating of metal-metal multiple bonds in these unsaturated binuclear carbonyl ion complexes. All of the binuclear first row transition metal carbonyl ion complexes in the present study are only metal-metal single or even half bonded except the Cr₂(CO)₉⁺ (n=7–9) cation complexes, which possess a linear Cr-C-O-Cr structural motif without a chromium-chromium bond. However, metal-metal multiple bonding is found to exist in unsaturated heteronuclear carbonyl anion complexes including UFe(CO)₃⁻ and OUF₆(CO)₃⁻, both of which are characterized to be U≡Fe triple bonded involving one electron-sharing σ bond and two Fe-to-U dative π bonds.

Density functional theory, in particular the hybrid B3LYP functional is shown here to be able to provide reliable predictions on the geometric structures and vibrational frequencies of these transition metal carbonyl cluster ions. Comparison of the experimental infrared spectra with the calculations allows definitive determination of the geometric and electronic structures of the metal carbonyl ions. The mass-selected infrared photodissociation spectroscopy in conjunction with density functional theory calculation is demonstrated here to be clearly a very powerful tool for transition metal carbonyl cluster chemistry.

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