Infrared Spectroscopy and Structures of Cobalt Carbonyl Cations, $Co(CO)_n^+$ ($n = 1-9$)[†]

A. M. Ricks,[§] J. M. Bakker,[‡] G. E. Douberly,[§] and M. A. Duncan*[,§]

Department of Chemistry, University of Georgia, Athens, Georgia 30602-2556, and FOM-Institute for Plasma Physics Rijnhuizen, P.O. Box 1207, Edisonbaan 14, NL-3430 BE Nieuwegein, The Netherlands

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Cobalt carbonyl cations of the form $Co(CO)_n^+$ ($n = 1-9$) are produced in a molecular beam by laser vaporization in a pulsed nozzle source. These ions, and their corresponding "argon-tagged" analogues, $Co(CO)_n(Ar)_m^+$, are studied with mass-selected infrared photodissociation spectroscopy in the carbonyl stretching region. The number of infrared-active bands, their frequency positions, and their relative intensities provide distinctive patterns allowing determination of the geometries and electronic structures of these complexes. $Co(CO)_5^+$ has a completed coordination sphere, consistent with its expected 18-electron stability, and it has the same structure (D_{3h} trigonal bipyramid) as its neutral isoelectronic analog $Fe(CO)_5$. The carbonyl stretches in $Co(CO)_5^+$ are less red-shifted than those in $Fe(CO)_5$ because of charge-induced reduction in the π back-bonding. $Co(CO)_{1-4}^+$ complexes have triplet ground states, but the spin changes to a singlet for the $Co(CO)_5^+$ complex.

Introduction

Transition metal carbonyls provide classic examples of metal−ligand bonding in Inorganic and Organometallic Chemistry.[1−3] Metal carbonyl complexes are employed as homogeneous catalysts for a variety of practical applications, including recently the production of single-walled carbon nanotubes.[4] Carbon monoxide is also a key ingredient in many heterogeneous catalysis systems and is the classic probe molecule for surface science studies.[5] Even in biological systems such as hemoglobin, carbon monoxide is important for its deleterious effects, competing with oxygen for binding at metal sites.[6] In all of these contexts, the carbonyl vibrational frequency (ν_{CO}) is used to diagnose the nature of the metal−ligand bonding, including its electronic structure and, on surfaces, the geometric binding arrangement.[1−3,5−9] The C−O stretch occurs in a frequency region isolated from many other molecular vibrations (2143 cm^{-1} for the free molecule),[10] and the shift of this frequency upon bonding to metal provides a sensitive indicator for the type of interactions present.[5−9] In the present study, we use IR spectroscopy of the carbonyl stretch vibration to examine the binding of CO ligands to cobalt cations in the gas phase.

Stable neutral transition metal carbonyl complexes have been studied extensively using infrared spectroscopy in the condensed phase and in the gas phase.[7,8,11−14] To test isoelectronic analogues, a variety of charged transition metal carbonyls have also been produced and studied in the condensed phase, as salts with corresponding counterions present.[15−18] Unsaturated metal carbonyls have been produced and isolated in rare gas matrices for IR spectroscopy.[9,19] Photoelectron spectroscopy of mass-selected anions has also provided new information about the ground states of small neutral carbonyls.[20−22] The frequency of the CO stretch (ν_{CO}) in all of these systems shifts systematically depending on the electronic structure and bonding, and these effects have been studied extensively with theory.[8,9,23−26] The direction and magnitude of the shift correlates well with the electron donating ability of the metal, with electron rich metals causing a large ν_{CO} red shift and electron poor metals causing a smaller red shift, or in extreme cases, a blue shift. These effects are traditionally attributed to the competition between σ-donation and π back-bonding in the metal carbonyl system. Sigma donation is thought to reduce the electron density in the partially antibonding CO σ molecular orbital and thus increases the C−O bond strength leading to a ν_{CO} blue shift. Conversely, π back-bonding from the metal to the purely antibonding π^* LUMO of CO results in a ν_{CO} red shift. This effect is illustrated in the isoelectronic series $Ni(CO)_4$, $Co(CO)_4^-$, and $Fe(CO)_4^{2-}$ in which the ν_{CO} stretching frequencies are respectively 2094, 1946, and 1799 cm^{-1}.[13,15,17] These covalent π and σ interactions are usually thought to dominate the nature of the metal carbonyl bond. However, recently it has been suggested that electrostatic interactions also play an important role in cationic systems.[25,26] This new thinking comes from recent ab initio calculations investigating the role of metal charge on the polarization and subsequent electron density distribution in the CO orbitals.[25,26] Unfortunately, there are few spectroscopic studies of isolated cationic carbonyls in which these effects can be explored.

Ionic metal carbonyl complexes have been studied extensively in mass spectrometry.[27,28] Many reactions have been documented, and dissociation energies have been measured.[29−32] Vibrational spectroscopy of anion and cation metal carbonyls have also been obtained by matrix isolation-IR spectroscopy, where the ion data could be compared with corresponding neutrals.[9,19] Gas phase spectroscopy studies of ionized carbonyls are quite limited. However, multimetal atom cluster carbonyls have been studied by photodissociation with infrared free electron lasers.[33−36] Recently we have studied the infrared spectra of various metal cation-ligand complexes in the gas phase using mass-selected ion infrared photodissociation spectroscopy.[37,38] In our first applications of this method to cation-carbonyls, we have investigated the $Au(CO)_n^+$ and $Pt(CO)_n^+$ systems.[39,40] In the present study, we use these same

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[†] Part of the "George C. Schatz Festschrift".

[*] To whom correspondence should be addressed. E-mail: maduncan@uga.edu.

[§] University of Georgia.

[‡] FOM-Institute for Plasma Physics Rijnhuizen.

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methods to study the cationic cobalt carbonyl complexes $Co(CO)_n^+$ for $n = 1-9$.

$Co(CO)_5^+$ is predicted to be stable because it satisfies the 18-electron rule and is isoelectronic to the well-known neutral $Fe(CO)_5$. Recently the salt $Co(CO)_5^+(CF_3)_3BF^-$ was synthesized and characterized using infrared and Raman spectroscopy and X-ray crystallography.[41] This study concluded that the $Co(CO)_5^+$ in the salt has D_{3h} symmetry with two infrared active bands at 2146 and 2120 cm^{-1}. In gas phase studies, the $Co(CO)_n^+$ dissociation energies for the $n = 1-5$ complexes have been previously measured by Armentrout and co-workers.[29d] The $Co(CO)_4^+$-CO bond energy was determined to be 0.68 eV (6290 cm^{-1}), and this demonstrated that up to five ligands were bound directly to the metal ion. The present study examines the infrared spectroscopy in the gas phase for both the small unsaturated $Co^+(CO)_n$ complexes ($n = 1-4$) and the larger complexes at and beyond the coordination sphere ($n = 5-9$). The infrared spectra provide new insight into the electronic structure and geometries of these fascinating complexes.

Experimental Section

$Co(CO)_n^+$ ions are produced in a pulsed nozzle laser vaporization source using the third harmonic of a pulsed Nd:YAG laser (355 nm; Spectra-Physics INDI-40). The laser is focused onto a rotating and translating 1/4 in. diameter cobalt rod mounted on the front of a pulsed nozzle (General Valve Series 9) in the so-called "cutaway configuration" which has been described previously.[37] The expansion gas is pure carbon monoxide (National Specialty Gas) at stagnation pressures of 3−10 atm. Mixed cluster ions containing argon, e.g., $Co(CO)_nAr_m^+$ are produced using argon-CO mixtures. The expansion is skimmed into a second chamber where positive ions are pulse-extracted into a homemade reflectron time-of-flight mass spectrometer. Ions of specific mass are selected by their flight time using pulsed deflection plates situated at the end of the first flight tube. These ions are excited at the turning point in the reflectron field with the tunable output of an infrared Optical Parametric Oscillator/Amplifier system (LaserVision) pumped by the fundamental of a Nd:YAG laser (1064 nm; Spectra Physics Pro 230). This laser system provides continuous tuning in the region 2000−4000 cm^{-1} with a line width of about 1 cm^{-1}. When the infrared laser is on resonance with a vibration of the complex, absorption and intramolecular vibrational energy relaxation (IVR) take place on a time-scale much smaller than that of the ion residency time in the reflectron (1−2 μs), leading to dissociation of the complex. Infrared spectra are obtained by monitoring the appearance of specific fragment ions as a function of the laser wavelength.

In support of the experimental work, Density Functional Theory (DFT) calculations were carried out to determine the structures and relative energetics of several possible isomers of $Co(CO)_n^+$ and $Co(CO)_nAr_m^+$, considering the singlet, triplet, and quintet states of each cluster size. The calculations were performed using the B3LYP functional[42,43] as implemented in the pcGAMESS computational code.[44] The Wachters+f basis set[45] was used on the Co atom while the DZP basis set[46] was used for the carbon and oxygen atoms and the 6-311+G* basis set was used for argon. The same functional and a similar basis set was used successfully by Schaefer and co-workers to calculate the structure and infrared frequencies for neutral $Fe(CO)_5$ which is isoelectronic to $Co(CO)_5^+$.[47] Calculations were done both with and without enforced symmetry to derive the structures for each complex.

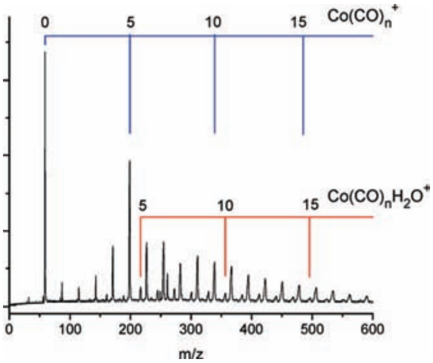

Figure 1. The mass spectrum of $Co(CO)_n^+$ clusters produced by our cluster source.

Results and Discussion

A mass spectrum of the $Co(CO)_n^+$ complexes produced by our source is shown in Figure 1. The largest complex peak corresponds to $Co(CO)_5^+$, indicating that this species is produced preferentially and suggesting that it is perhaps more stable than others. This is exactly the cation expected to be stable, as it is isoelectronic to neutral $Fe(CO)_5$. The complexes larger than this presumably do not have their additional CO ligands coordinated directly to the metal, but bound externally by weaker electrostatic forces (charge-dipole, charge-induced dipole, etc.). These larger complexes would likely not be stable in a room temperature environment, but they are produced efficiently here because of the cold supersonic beam conditions.

Further insight into the ligand binding energetics in these systems can be obtained by their relative tendencies to dissociate upon infrared excitation, and by the fragmentation patterns that result. We find that the small $Co(CO)_n^+$ complexes ($n = 1-4$) do not fragment upon infrared excitation. This is consistent with their strong binding energies (1.80, 1.58, 0.85, 0.78 eV, respectively, for elimination of the last CO from $n = 1-4$), which have been measured previously by Armentrout and co-workers.[29d] The energy of IR photons in the region of the C−O stretching fundamental near 2200 cm^{-1} is only about 0.27 eV. Therefore, it makes sense that the small complexes cannot be photodissociated in this way.

The infrared fragmentation mass spectra of the $Co(CO)_n^+$ ($n = 5-9$) complexes are shown in Figure 2. These spectra are obtained by taking the difference between the mass spectrum of a selected complex with the infrared photodissociation laser on versus off. The negative peak indicates the depletion of the selected parent ion by its dissociation, and the positive peaks indicate the fragments produced. For each cluster size this so-called breakdown spectrum was obtained with the laser set to the maximum absorbance of that particular cluster. As shown, beginning at $n = 5$, we can detect some photodissociation. The lower signal obtained for this cluster indicates a poor fragmentation yield, consistent with the high binding energy determined for this complex by Armentrout and co-workers (0.78 eV; 6290 cm^{-1}). Again, single photon dissociation is not possible, and the signal observed must be coming from either a small amount of multiphoton absorption, or from some absorption by a "warm" fraction of the ions whose internal energy was not quenched effectively by collisions in the growth process. Multiphoton absorption is not expected to be very efficient with the laser pulse energies here (about 1 mJ/pulse). Residual internal energy could add to the photon energy, making photodissociation possible below the one-photon threshold, but this signal would also not be large because the warm ions

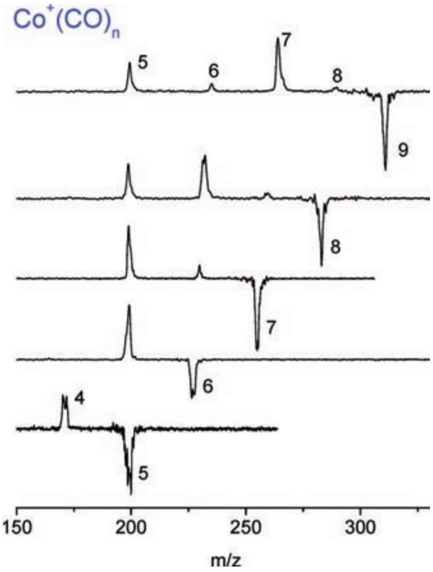

Figure 2. The photofragmentation mass spectra of $Co(CO)_n^+$ species.

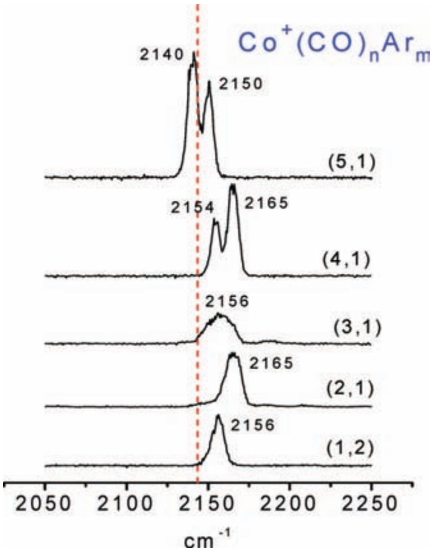

Figure 3. The infrared photodissociation spectra of the small $Co(CO)_n^+(Ar)_m$ complexes, detected by the elimination of argon.

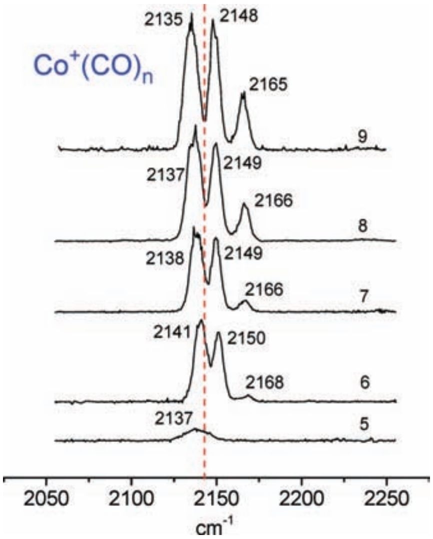

Figure 4. The infrared photodissociation spectra of the larger $Co(CO)_n^+$ complexes, detected by the elimination of CO.

represent a small fraction of the total population. The $n = 6$ cluster fragments much more efficiently, producing only the $n = 5$ species. This is consistent with a significantly lower binding energy for the last CO molecule in this complex, which makes its elimination possible by one-photon absorption. Because the $n = 5$ species is the expected closed shell complex, it makes sense that $n = 6$ would have one external CO ligand not coordinated directly to the metal cation, but bound by weak electrostatic interactions. Consistent with this, species larger than $n = 5$ were not produced in the Armentrout experiment, presumably because the ions were thermalized to room temperature.[29d] All the clusters larger than $n = 6$ should also have external CO molecules, and they all fragment efficiently. These larger species eliminate multiple CO ligands, eventually terminating at the $n = 5$ species. This is again consistent with weak binding for the outer ligands and the closed coordination sphere and higher binding energy for the $n = 5$ species.

To investigate the spectroscopy of these systems, we measure the wavelength dependence of these fragmentation processes. Because IR excitation cannot dissociate the smaller clusters ($n \leq 5$) efficiently, we study these systems with "inert gas tagging".[37,38,48−51] In this method, we produce mixed complexes of the form $Co(CO)_n(Ar)_m^+$. Photoexcitation of the ligand vibrations in these tagged complexes, followed by IVR, can lead to efficient elimination of argon, which then provides a more efficient way to detect the IR spectrum. In many ion-molecule complexes, the binding of a rare gas such as argon has a negligible effect on the structure and spectrum of the complex. In other systems, if argon binds strongly, it can act essentially as a ligand and the tagged complex is strongly perturbed compared to the neat system. We therefore exercise due caution in interpreting these spectra and use computations to investigate the structures and spectra of both the tagged and the neat systems (see below).

Figure 3 shows the spectra of the $n = 1-5$ complexes measured by tagging with argon. For the $n = 2-5$ complexes, tagging with a single argon is enough to achieve efficient photodissociation. However, no photodissociation of the $Co(CO)Ar^+$ complex was observed. This is understandable, because argon binds relatively strongly to the cobalt cation; the dissociation energy of diatomic $CoAr^+$ has been measured by Brucat and co-workers to be 4111 cm^{-1}.[52] As the $Co(CO)Ar_2^+$ complex did exhibit IR induced fragmentation, we have measured and present its spectrum. The dashed vertical line shows the position of the stretch in the isolated CO molecule at 2143 cm^{-1}. As shown, the resonances for the $Co(CO)_n(Ar)_m^+$ complexes all occur quite close to this value, i.e., there is only a small shift from the free molecule frequency. In the small complexes, the shifts are to higher frequency, but the two bands for the $n = 5$ complex are centered around the free-CO frequency. The $n = 1-3$ spectra have a single band, which is broader and weaker for the $n = 3$ complex than it is for the $n = 1,2$ species. The $n = 4$ and 5 spectra both have a doublet band structure. We investigate these systems further below with DFT computations on the complex structures, spin states, and spectra.

The infrared photodissociation spectra for the $Co(CO)_n^+$ ($n = 5-9$) complexes could be measured without argon tagging, and these are shown in Figure 4. Although it occurs in about the same position, the spectrum for the $n = 5$ complex here is broader than the one obtained with tagging and it does not contain the doublet seen in Figure 3. This make sense because one-photon dissociation is not possible for this cluster, as

TABLE 1: The Structures, Electronic Ground States, and Energetics Computed for $Co(CO)_n^+$ and $Co(CO)_n(Ar)_m^+$ Complexes with DFT[a]

complex	state/structure	relative energy	E[$Co(CO)_n^+$-CO] (exp)
$Co(CO)^+$	$^3C_{\infty v}$	0.0	41.2 (41.5 ± 1.6)
	$^1C_{\infty v}$	+15.7	8.7
$Co(CO)_2^+$	$^3D_{\infty h}$	0.0	38.9 (36.4 ± 2.1)
	$^1D_{\infty h}$	+15.7	39.5
$Co(CO)_3^+$	$^3C_{2v}$	0.0	26.5 (19.6 ± 2.7)
	$^3C_{3v}$	+2.5	26.5
	$^3D_{3h}$	+13.0	15.7
	$^1C_{2v}$	+25.4	12.6
$Co(CO)_4^+$	$^3C_{2v}$	0.0	38.9 (18.0 ± 1.4)
	$^1D_{4h}$	+7.5	26.6
$Co(CO)_5^+$	$^3C_{3v}$	+7.5	23.7 (18.0 ± 1.2)
	$^1D_{3h}$	0.0	32.0
$Co(CO)_6^+$	^3O_h	+2.6	10.4
	$^1C_{2v}$	0.0	1.8

[a] Experimental binding energies (in parentheses) are from the work of Armentrout and coworkers.[29d]

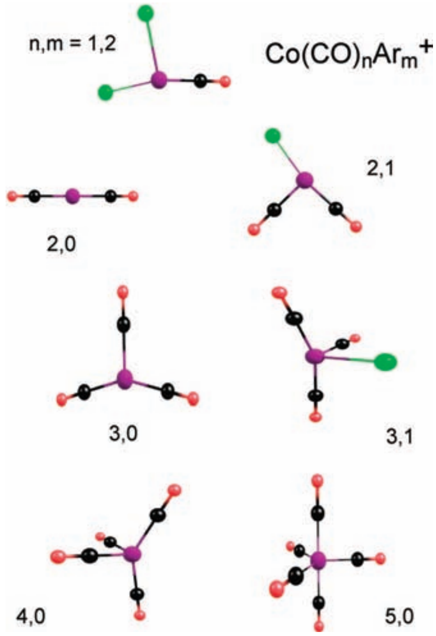

Figure 5. The structures for $Co(CO)Ar_2^+$, $Co(CO)_2^+$ and $Co(CO)_2^+Ar$, $Co(CO)_3^+$ and $Co(CO)_3^+Ar$, $Co(CO)_4^+$, and $Co(CO)_5^+$ complexes determined with density functional theory. The argon changes the structures of the $n = 1$ and 2 complexes significantly, but has a negligible effect on the larger complexes.

discussed above. Therefore, the tagged $n = 5$ complex is expected to give the most accurate representation of its spectrum. Beginning with the spectrum for the $n = 6$ complex, the dissociation efficiency is much greater, consistent with a one-photon process, as expected for species with weakly bound external CO molecules. In each of the $n = 6-9$ spectra, two main peaks are present while a third much weaker band is located further to the blue. The positions of all of these bands remain virtually the same for different cluster sizes, except that the intensity of the weak band to the blue increases for the larger complexes. The doublets here also occur at essentially the same frequencies as the two bands seen for $Co(CO)_5^+Ar$. This is the behavior expected if the $n = 5$ is the core ion for this system, with a complete coordination about the metal ion, and subsequent CO ligands are bound weakly. The spectra for the $n = 6-9$ species therefore represent CO-solvated $Co(CO)_5^+$ ions. The weak band at higher frequency is only present for the larger complexes, its position is essentially unchanged for different clusters, and its intensity grows with cluster size. This band is therefore assigned to the CO stretch for the external CO molecules. Vibrations for external "solvent" molecules have been seen for many of the other cation-molecular complexes that we have studied previously.[37,38]

To further elucidate these spectra, we have performed DFT calculations on $Co(CO)_n^+$ for $n = 1-7$. Complete details on all the calculated structures, energetics, and spin states are provided in the Supporting Information for this paper. A summary of the most relevant data is presented in Table 1. Previous computational studies on $Co(CO)_n^+$ complexes were reported by Barnes and Bauschlicher[23] (for $n = 1$ and 2) and by Huo et al.[24] (for $n = 1-5$). We have reinvestigated various isomers and spin states for each complex and have done the corresponding argon complexes at the same level of theory to make the most appropriate predictions for the spectra that we measure. The computed lowest energy structures are shown in Figure 5 for selected examples of these complexes. In the case of the $n = 1-3$ complexes, tagging changes the structure noticeably, and so we show structures for both the tagged and neat species. The $n = 4$ and 5 complexes add argon without significantly changing the structures. The excellent signal levels achieved in this photodissociation experiment can also be understood with these theoretical results. The calculated intensities of the CO stretches here are generally >500 km/mol (see Supporting Information). Additionally, the binding energy of the external CO molecules (calculated to be 627 cm^{-1}; see Supporting Information) is also low enough to make efficient photodissociation possible when such external ligands are present.

For the most part, the neat $n = 1-5$ species here have structures consistent with those computed previously.[23,24] Barnes and Bauschlicher found linear triplet ground states for both the $n = 1$ and 2 complexes,[23] while Huo et al. found a slightly bent minimum for $n = 1$ in addition to the $C_{\infty v}$ structure.[24] We find linear structures for both of these complexes, with the singlet states lying much higher in energy than the triplets for both. The monoargon complex of the $n = 1$ species is also linear, and addition of a second argon (necessary for the photodissociation) produces a C_s structure, as shown in the figure. Argon tagging has a significant effect on the $n = 2$ complex, distorting the linear system to a strongly bent one, with the argon acting essentially as a third ligand. The $n = 3$ complex has a triplet C_{2v} structure, as found previously by Huo et al.[24] The D_{3h} structure lies much higher than this, but a C_{3v} structure lies at only slightly higher energy than the C_{2v} species. The $n = 4$ complex has a triplet C_{2v} structure like that found by Huo et al.[24] Again consistent with their work, we find that the $n = 5$ complex has a trigonal bipyramid D_{3h} structure, but as a *singlet*. The singlet-triplet energy difference is computed to be 7.5 kcal/mol for the $n = 4$ complex, with the triplet more stable. The spacing is the same, but the order is reversed for the $n = 5$ species. Therefore, the $n = 1-4$ complexes are all triplets, but the spin changes to singlet on going from $n = 4$ to 5. The calculated structure of $Co(CO)_5^+$ is also in good agreement with the structure measured in the $Co(CO)_5^+(CF_3)_3BF^-$ salt using X-ray crystallography.[41] No minimum could be found on the singlet potential energy surface for a six-coordinate $Co(CO)_6^+$ complex. Instead, all starting six-coordinate structures converged to structures with a central D_{3h} $Co(CO)_5^+$ complex with an external CO molecule. This is consistent with the conclusion drawn above that five CO molecules complete the first coordination sphere around the cobalt cation. Interestingly, $Co(CO)_6^+$

TABLE 2: The Vibrational Frequencies Computed (Scaled by 0.9731) and Measured for $Co(CO)_n^+$ and $Co(CO)_n(Ar)_m^+$ Complexes

complex	theory Huo[24]	present theory	exp Andrews[19g]	this exp
$Co\text{-}CO^+$	linear: 2188.3 bent: 2216.3	2190.7	2165.5	
$Co(CO)Ar^+$		2207.0		
$Co(CO)Ar_2^+$		2171.1		2156
$Co(CO)_2^+$	$D_{\infty h}$: 2176.7	2173.9	2168.9	
$Co(CO)_2Ar^+$		2153.4, 2190.4		2165
$Co(CO)_3^+$	C_s: 2165.8, 2168.3	2181.2, 2181.5		
$Co(CO)_3Ar^+$		2161.6, 2160.6		2156
$Co(CO)_4^+$	C_{2v}: 2156.6, 2163.8 D_{4h}: 2143.9	2157.8, 2163.2		
$Co(CO)_4Ar^+$		2155.6, 2161.6, 2161.9		2154, 2165
$Co(CO)_5^+$	D_{3h}: 2133.7, 2150.1	2140.0, 2154.1		
$Co(CO)_5Ar^+$		2140.1, 2140.6, 2154.4		2140, 2150

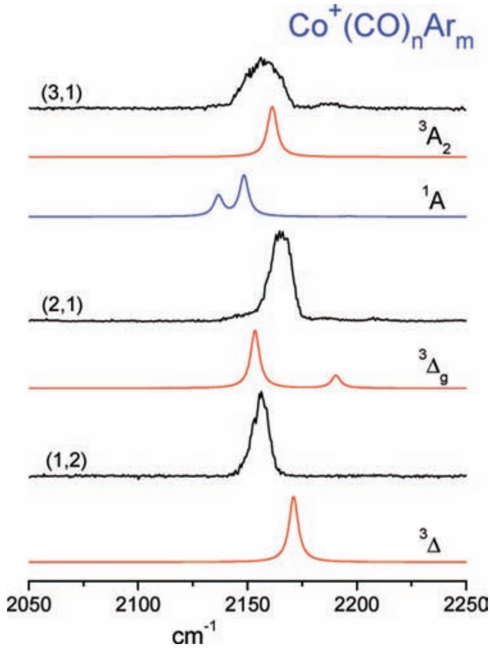

Figure 6. The infrared spectra of the smaller $Co(CO)_n^+$ complexes compared to the spectra predicted by theory.

did converge to a hexacoordinate O_h structure as a triplet, even when the input was similar to that of the singlet $Co(CO)_6^+$. At the level of theory employed, the singlet D_{3h} $Co(CO)_5^+$ with a single external CO is computed to be lower in energy than the hexacoordinate triplet O_h $Co(CO)_6^+$, but only by 2.6 kcal/mol. For all of these $Co(CO)_n^+$ complexes, the quintet was always significantly higher in energy than the triplet or singlet species and is therefore ruled out from further consideration.

Table 2 provides a comparison of the band positions for the carbonyl stretches measured for these complexes to those computed by theory in both the previous and present work. As shown in the table, argon tagging does induce some noticeable shifts in these spectra, but the shifts are much greater for the n = 1−3 complexes than they are for the n = 4 and 5 systems. This is consistent with a strong binding of argon in the small complexes, where it can essentially occupy a vacant ligand site. The computed frequencies for the untagged complexes in our work differ slightly from those in the work of Huo et al. (using DFT/B3LYP with the 6-311+G(d) basis on C and O and the Wachters-Hay[45] basis plus one polarization function and diffuse functions on Co),[24] which is understandable because of the different basis sets and scaling employed. Figure 6 shows the comparison of the experimental spectra for the n = 1=3 complexes with those predicted by theory for the most stable argon-tagged structures of these complexes. The calculated frequencies are scaled by 0.9731 and are given a 5 cm^{-1} FWHM Lorentzian line shape for comparison to the experimental spectra. This scaling factor was chosen to make the calculated and experimental $Co(CO)_5^+$ bands at 2140 cm^{-1} coincide and is in line with scaling factors recommended for the B3LYP functional.[53] As shown, $Co^+(CO)$ has a computed frequency of 2191 cm^{-1}, while the singly tagged complex has a computed value that is higher at 2207 cm^{-1}. The trend is reversed for $Co(CO)Ar_2^+$, which is computed to have a frequency further to the red from the isolated complex at 2171 cm^{-1}. For comparison to this, the experiment on $Co(CO)Ar_2^+$ measures a single CO stretch at 2156 cm^{-1}, which is still further to the red. The linear structure for $Co(CO)_2^+$ has a computed frequency of 2174 cm^{-1}, which is quite close to the value of 2169 cm^{-1} measured by Zhou and Andrews in a neon matrix experiment.[19g] However, the $Co(CO)_2Ar^+$ complex is calculated to have a strongly distorted C_s structure, with the carbonyl groups bent strongly away from linear. This bent structure therefore has two IR-active modes at 2153 and 2190 cm^{-1}. In contrast to this, the experimental spectrum for this singly tagged species has only one band at 2165 cm^{-1}, which is within 4 cm^{-1} of the neon matrix result for the untagged species. The single band is consistent with a complex that is not distorted significantly from linear, and the frequency so close to the matrix value is also consistent with this. Apparently, tagging actually induces a relatively minor perturbation on this complex, and this effect is greatly overestimated by the level of theory employed. For the n = 3 complex, we show the computed spectra for both the singlet and triplet species, even though the computed energy difference for these is significant. As shown, only the triplet species has the single band predicted by theory, and the position measured for this band is in good agreement with the predicted value.

Figure 7 presents the comparison between theory and experiment for the n = 4−6 complexes. Table 2 shows that the neat $Co(CO)_4^+$ complex and the tagged $Co(CO)_4Ar^+$ species have essentially the same frequencies, consistent with a weak binding interaction for the tag atom. The neat complex has the triplet C_{2v} structure predicted before by Huo et al.,[24] while the tagged complex has a symmetry lower than this because of the presence of the argon. The latter has three IR-active modes, but the splitting induced by the reduced symmetry is much smaller than our resolution, and so we detect only two bands in the experiment. The experimental position of these bands and their relative intensities are in good agreement with the predicted values. As shown in the figure, the singlet for this complex should have a single band in its spectrum, and this clearly does not agree with the experiment. $Co(CO)_4^+$ therefore has a triplet spin state. The n = 5 complex again has nearly the same vibrations predicted for the neat and tagged species, with a slight reduction in symmetry induced by the argon. Again, this splitting is too small to resolve, and we detect only two bands. The figure here again shows the spectra predicted for the lowest triplet and singlet states, where now the theory for the first time indicates that the *singlet* lies at lower energy. Indeed, the position and intensities of the experimental bands also agree nicely with the pattern predicted for the singlet D_{3h} structure.

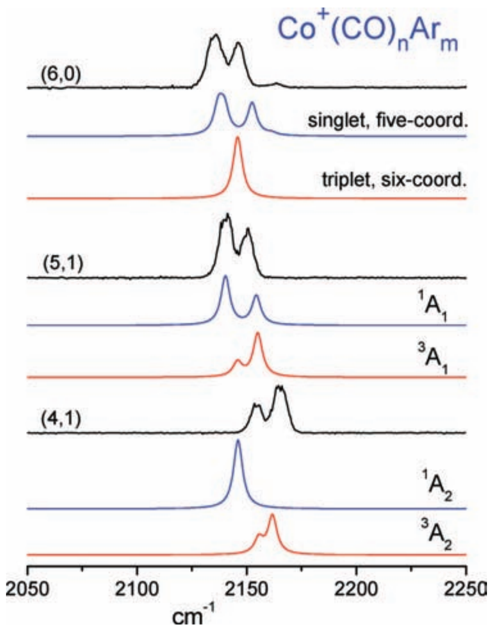

Figure 7. The infrared spectra of the larger $Co(CO)_n^+$ complexes compared to the spectra predicted by theory.

The triplet here also has a two-band spectrum, but it is more shifted and the relative intensities of the two bands are reversed compared to the experiment. Therefore, the infrared spectrum confirms the change in spin predicted on going from the $n = 4$ to the $n = 5$ species. The reduction in spin that occurs as additional ligands are added around a metal center is one of the familiar concepts in ligand field theory.[2] However, there are few systems like the present one in which this effect can be observed for the full series of ligand additions up to the completed coordination.

We assign the peak at 2140 cm^{-1} in the $Co(CO)_5Ar^+$ spectrum to the doubly degenerate e′ in-plane asymmetric CO stretch of the $Co(CO)_5^+$ core, which represents a 20 cm^{-1} blue-shift from the value seen previously in the salt.[41] The addition of argon to the $Co(CO)_5^+$ core formally splits the doubly degenerate e′ modes into two nondegenerate a′ and a″ modes, however this splitting is calculated to be only ~0.5 cm^{-1} and we are not able to resolve it. We assign the peak at 2150 cm^{-1} to the a_2'' out-of-phase stretching of the axial carbonyls on the core $Co(CO)_5^+$ ion, which is only 4 cm^{-1} to the blue from the value obtained in the $Co(CO)_5^+(CF_3)_3BF^-$ salt.[41] The iron pentacarbonyl complex, which is isoelectronic to $Co(CO)_5^+$ and also has D_{3h} symmetry,[14] has corresponding e′ and a_2'' vibrations at 2013 and 2034 cm^{-1}.[13] Both of these are at much lower frequencies than the bands seen here. The red shifts of the vibrations for the neutral relative to the isoelectronic cation are most likely due to the differences in π back-bonding from the metal d orbitals into the antibonding π^* LUMO of the CO ligands. The charged cobalt binds its d electrons more strongly than the neutral iron, thus inhibiting the back-bonding, and leading to less red-shifting in the C−O stretches. A similar kind of charge dependence on π back-bonding has been documented previously for the isoelectronic series $Ni(CO)_4$, $Co(CO)_4^-$, and $Fe(CO)_4^{2-}$, in which ν_{CO} stretching frequencies are respectively 2094, 1946, and 1799 cm^{-1}.[13,15,17] In this series, the negative ions have *greater* back-bonding, and larger red shifts, than the corresponding neutral. Our results here, which allow the $Co(CO)_5^+$ cation to be compared to the isoelectronic $Fe(CO)_5$ species, are qualitatively consistent with the interpretation of these previous results.

Because we obtain spectra for complexes beyond the stable five-coordinate ion, we can also investigate the possibility of a less-stable six-coordinate species. As mentioned above, the triplet hexa-carbonyl species is computed to lie quite close in energy to a singlet penta-carbonyl with one external CO. The top three traces in Figure 7 show the experimental spectrum for $Co(CO)_6^+$ in the CO-loss channel compared to the spectra computed for the five- and six-coordinate species. As shown, the spectrum measured is completely consistent with the singlet $Co(CO)_5^+$-CO structure. The hexa-coordinate spectrum would have a single band, and this would occur at about the same frequency as the higher frequency band measured for the five-coordinate species. Therefore, we cannot rule out the presence of a small amount of triplet $Co(CO)_6^+$. But because the intensity ratios in the spectrum match those computed for the solvated $Co(CO)_5^+$, the amount of triplet $Co(CO)_6^+$, if any, would have to be small. However, the binding energy of the triplet $Co(CO)_6^+$ species is computed to be larger than the photon energy (see Table 1), and so it is also conceivable that this species is present but not detected by the IR. On the other hand, the larger species ($n > 6$) have the same spectrum as the $n = 5$ and 6 species, suggesting that there is not any large amount of another core ion present.

Because the $n = 5$ complex can now be regarded as the "core" ion for this system, and the $n = 6$ ion represents a singly CO-solvated version of this, we can presume that the larger clusters are also CO-solvated $Co(CO)_5^+$ complexes. Consistent with this, the spectra for the $n = 7-9$ complexes have two main bands at virtually the same positions as those for the $n = 6$ and the tagged $n = 5$ species. As the $Co(CO)_n^+$ cluster size increases, the two main peaks located at 2140 and 2150 for $Co(CO)_5^+$ are at 2140 and 2151 cm^{-1} in the $Co(CO)_6^+$ spectrum. These gradually split further apart and shift slightly to the red until they are located at 2134 and 2148 cm^{-1} in the $Co(CO)_9^+$ spectrum.

As we have discussed for other systems, in a complex where there are more ligands than binding sites on the metal, the excess molecules can bind to the surface of the fully coordinated complex and give rise to spectral bands similar to those of the free molecule. In the $Co(CO)_6^+$ spectrum (Figure 4) this "surface" CO stretch is located at 2168 cm^{-1}, and this changes slightly with cluster size to a value of 2165 cm^{-1} for $Co(CO)_9^+$. These frequencies are 22−25 cm^{-1} to the blue from the gas phase value of 2143 cm^{-1} for free CO. This shift is in contrast to the much smaller blue shifts (~5 cm^{-1}) we have seen previously for surface CO_2 molecules in corresponding metal-CO_2 systems.[54] Apparently, surface CO molecules are perturbed more than surface CO_2 molecules in these situations.

Goldman and Krogh-Jespersen have explored the polarization of CO molecules adjacent to a nearby charge.[25] The interaction of CO with a spherically symmetric point charge was investigated computationally by placing a proton with only a single diffuse *s* basis function near the carbon end of a CO molecule. The only interactions possible in such a complex are σ-donation and electrostatic polarization, as the π^* orbital of CO does not have the correct symmetry to bond with the spherically symmetric point charge. By varying the proton-carbon distance, Goldman and Krogh-Jespersen determined that the interaction in this system was dominated by the electrostatics and that the σ-bonding was quite small. A blue shift, consistent with a stronger C−O bond, was attributed to a more balanced electron distribution in the CO bonding orbitals that was achieved by the polarization. Interpolating from these published results to the $Co(CO)_5^+$-CO distance of 4.1 Å calculated in this work (see Supporting Information), the surface CO frequency is predicted to be blue-shifted 17 cm^{-1} from the gas phase value, compared to the larger shift of 22−25 cm^{-1} seen experimentally. The $Co(CO)_5^+$ cation is not a point charge, and thus the shift computed on this basis should overestimate the real value, but it in fact underestimates it. Thus, although a qualitative blue shift can be explained by polarization of the CO, this alone does not seem to be enough to explain the magnitude of the shift observed. In our work on metal ion-CO_2 complexes, we also noted that a physical effect of ligand-surface repulsion could effectively steepen the outer wall of the intermolecular potential, which would also lead to an increase in the surface ligand frequency.[54] It is conceivable that a combination of both of these effects are at work on the surface CO vibrations. To our knowledge, this is the first gas phase spectroscopy that could investigate these interactions for external CO molecules. However, additional examples are anticipated as we extend these studies to other gas phase metal carbonyls.

Conclusions

Cobalt carbonyl cations of the form $Co(CO)_n^+$ ($n = 1-9$), and their corresponding "argon-tagged" analogues, $Co(CO)_n(Ar)_m^+$, were produced and studied with mass-selected infrared photodissociation spectroscopy and density functional theory. Each of these complexes has one or more carbonyl stretching bands near those of the free CO molecule. The number of infrared-active bands, their frequency positions, and their relative intensities provide distinctive patterns allowing determination of the geometries and electronic structures of these complexes. $Co(CO)_5^+$ has a completed coordination sphere, consistent with its expected 18-electron stability, and it has the same structure (D_{3h} trigonal bipyramid) as its neutral isoelectronic analog $Fe(CO)_5$. The carbonyl stretches in $Co(CO)_5^+$ are less red-shifted that those in $Fe(CO)_5$ because of charge induced reduction in the π back-bonding. The smaller $Co(CO)_{1-4}^+$ complexes have triplet ground states, but the spin changes to a singlet for the $Co(CO)_5^+$ complex. The carbonyl stretch for external CO ligands in the larger complexes ($n > 5$) is somewhat blue-shifted from the free molecule value. This effect is investigated with a simple electrostatic model applied previously to other cation-carbonyl systems, which underestimates the shifts seen. These IR spectroscopy measurements provide unprecedented details about metal-ligand interactions and also the solvation that occurs in external ligand layers.

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Supporting Information Available: The Supporting Information for this manuscript contains the full details of the DFT computations done in support of the spectroscopy here, including the structures, energetics, and vibrational frequencies for each of the structures considered. This material is available free of charge via the Internet at http://pubs.acs.org.

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