Infrared Spectroscopy of Gas-Phase \( M^+(CO_2)_n \) (\( M = \text{Co, Rh, Ir} \)) Ion–Molecule Complexes

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Supporting Information

ABSTRACT: The structures of gas-phase \( M^+(CO_2)_n \) (\( M = \text{Co, Rh, Ir} \); \( n = 2–15 \)) ion–molecule complexes have been investigated using a combination of infrared resonance-enhanced photodissociation (IR-REPD) spectroscopy and density functional theory. The results provide insight into fundamental metal ion–CO\(_2\) interactions, highlighting the trends with increasing ligand number and with different group 9 ions. Spectra have been recorded in the region of the CO\(_2\) asymmetric stretch around 2350 cm\(^{-1}\) using the inert messenger technique and their interpretation has been aided by comparison with simulated infrared spectra of calculated low-energy isomeric structures. All vibrational bands in the smaller complexes are blue-shifted relative to the asymmetric stretch in free CO\(_2\), consistent with direct binding to the metal center dominated by charge–quadrupole interactions. For all three metal ions, a core \( [M^+(CO_2)]_2 \) structure is identified to which subsequent ligands are less strongly bound. No evidence is observed in this size regime for complete activation or insertion reactions.

I. INTRODUCTION

There has been much interest in carbon dioxide (CO\(_2\)) activation in synthetic chemistry over the past two decades.\(^{1–3}\) Most practical CO\(_2\) transformations involve metal-based catalysts, and detailed investigations are required to better understand the fundamental interactions involved. In this context, gas-phase studies of metal–ion complexes have a key role to play in elucidating important aspects of metal–ligand bonding, metal ion solvation, and molecular activation.\(^{4,5}\) Such studies can provide valuable insight into the salient features of reaction mechanisms, energetics, kinetics, etc., free from the perturbing effects of solvents, counterions, aggregates, or surface inhomogeneities encountered in situ.\(^{6–7}\)

Number densities of gas-phase metal–ion complexes produced by laser ablation are typically too low to be probed directly by traditional direct absorption spectroscopic methods. However, modern laboratory-based intense, tunable infrared systems can now produce IR light in the wavelength range 1.35–5 \( \mu \)m. This has, in turn, driven the development of novel action spectroscopies such as infrared resonance enhanced photodissociation (IR-REPD), which provides information on geometric structures of isolated, gas-phase metal ion–ligand complexes. IR-REPD measurements on metal-ion containing complexes were first performed by Lisy et al., who studied alkali metal–ion complexes with ligands including H\(_2\)O, CH\(_3\)OH, and CH\(_4\).\(^{8–15}\)

CO\(_2\) complexes with main group (Mg\(^+\), Al\(^+\), and Si\(^+\))\(^{16–18}\) and first-row transition metal cations\(^{19–24}\) have been studied by Duncan and co-workers,\(^{25}\) whereas Zhou and co-workers have investigated Ti\(^+\)(CO\(_2\))\(_n\) clusters.\(^{24}\) Spectroscopic studies show a systematic blue shift of the fundamental transition associated with the asymmetric stretching mode of complexed CO\(_2\) relative to that of free CO\(_2\). The binding of the CO\(_2\) ligands to the metal cation center occurs almost exclusively through a charge–quadrupole interaction via one of the oxygen atoms, with little evidence of charge transfer.\(^{25}\) As the number of CO\(_2\) ligands increases, multiple bands are observed, including some that appear close to the wavenumber of free CO\(_2\), indicating the presence of second solvent-sphere or more weakly–bound ligands. Such observations can highlight characteristic CO\(_2\) coordination numbers by comparison of experimental IR-REPD spectra with simulated IR spectra for low-lying structures calculated typically via density functional theory (DFT).

Previous studies of \( M^+(CO_2)_n \) complexes have determined linear structures for \( M' = \text{Fe}^+ \) and Ni\(^+\) for \( n = 2 \).\(^{19,22}\) By contrast, Mg\(^+(CO_2)_2\), Al\(^+(CO_2)_2\), and Si\(^+(CO_2)_2\) structures are nonlinear, with the \( n = 3 \) variants typically trigonal pyramidal (apart from trigonal planar Si\(^+(CO_2)_3\)).\(^{16–18}\) The structures of small \( V^+(CO_2)_2 \) complexes are less clear, with evidence of low-symmetry structures and/or perturbation by the argon tag.\(^{22}\)

A coordination number of 4 has been observed for CO\(_2\) ligands around Ni\(^+\) and V\(^+\), and \( n = 4–7 \) for Fe\(^+\).\(^{20,22,23}\) No clear coordination number for Mg\(^+\), Al\(^+\), and Si\(^+\) was observed,\(^{16–18}\) although an increased photodissociation yield is observed for \( n > 2 \) in Al\(^+(CO_2)_2\), and Si\(^+(CO_2)_2\).
In providing structural information about the complexes interrogated, IR-REPD studies have also revealed evidence of various intracenter reactions such as oxide–carbonyl formation in Ni(\textsuperscript{+}CO\textsubscript{2})\textsubscript{6}, Si(\textsuperscript{+}CO\textsubscript{2})\textsubscript{9}, and Ti(\textsuperscript{+}CO\textsubscript{2})\textsubscript{9} clusters, and oxalate-type anion formation in large V\textsuperscript{+}(\textsuperscript{+}CO\textsubscript{2})\textsubscript{11} complexes.\textsuperscript{18,23,24,26}

By contrast with the cationic species, IR-REPD studies of anionic, M\textsuperscript{−}(\textsuperscript{−}CO\textsubscript{2})\textsubscript{6} complexes (M = Au, Ag, Co, and Ni)\textsuperscript{27−31} by Weber et al. reveal considerable CO\textsubscript{2} activation marked by red shifts in vibrational frequencies of several hundred cm\textsuperscript{−1}. In the case of Co\textsuperscript{3−}(\textsuperscript{−}CO\textsubscript{2})\textsubscript{6} complexes, the vibrational frequency of directly bound ligands is red-shifted to ca. 1750 cm\textsuperscript{−1} from the free CO\textsubscript{2} asymmetric stretch vibrational frequency at 2349 cm\textsuperscript{−1}. This weakening of the CO\textsubscript{2} bond enhances the chances of bond–insertion reactions leading to inserted OCo\textsuperscript{2−}(CO)\textsuperscript{−} complexes as putative global minima.\textsuperscript{30}

Here, we report the results of an IR-REPD spectroscopy study of gas-phase M\textsuperscript{+}(\textsuperscript{+}CO\textsubscript{2})\textsubscript{6} complexes (M = Co, Rh, Ir, n = 2−15) designed to elucidate trends in cluster structure down the group 9 metal ions. For the smaller complexes (n ≤ 10), the inert messenger or rare gas tagging technique has been employed whereby loss of a weakly–bound argon atom provides a mass spectrometric signature of photon absorption. This technique has been exploited previously by our group in studies of larger naked and decorated transition metal clusters.\textsuperscript{37−45} For the larger M\textsuperscript{+}(\textsuperscript{+}CO\textsubscript{2})\textsubscript{6} complexes (n > 10), however, the intensity of the Ar-tagged species is too low and Ar-tagged complexes simultaneously, in most cases we observe no qualitative difference in the spectra of the two, lending support to the proposition that the argon tag is indeed inert and does not significantly perturb the cluster structure.

II. EXPERIMENTAL SECTION

The laser ablation/time-of-flight instrument used to perform the experimental work is new and a brief introduction is warranted. Figure 1 shows a schematic of the entire instrument.

![Figure 1. Schematic of the overall experimental setup used for the study of gas-phase M\textsuperscript{+}(\textsuperscript{+}CO\textsubscript{2})\textsubscript{n}−Ar complexes. The “cutaway” ablation block is based on the design of Duncan and co-workers and facilitates the formation of single metal ion complexes.](image)

used for the IR-REPD experiments. It comprises two differentially pumped chambers: (i) a source chamber, containing a simple laser ablation source and (ii) a detection chamber, consisting of a commercial Wiley–McLaren time-of-flight (TOF) mass spectrometer (R. M. Jordon Co., Inc.). The two regions are maintained at background pressures of ca. 1 × 10\textsuperscript{−7} mbar using turbomolecular pumps backed by two individual rotary pumps.

The laser ablation source, used to generate the various M\textsuperscript{+}(\textsuperscript{+}CO\textsubscript{2})\textsubscript{n}−Ar species of interest is a variant of the tapered ablation block source used by Duncan et al.\textsuperscript{34} The absence of a cluster chamber minimizes formation of metal clusters, leading to efficient formation of Ar-tagged CO\textsubscript{2}-complexed metal atomic cations in an essentially free expansion. The ablation target disk (Co (1 mm thick) and Rh (0.5 mm thick), Sigma Alrich 99.95%; Ir (0.125 mm thick), Goodfellow 99.9%) is continuously rotated to refresh the surface. Laser ablation occurs at 10 Hz using ca. 5 mJ of 532 nm light from a frequency-doubled pulsed Nd:YAG laser (Continum MiniLite).

The metal vapor generated by ablation is entrained in a pulse of argon gas seeded with a low percentage of carbon dioxide (typically 0.1−1%), delivered by a pulsed solenoid valve (Parker-Hannifin, Series 9) from a typical backing pressure of 6 bar. During experimentation, the pressure in the source (detection) chamber rises to ca. 1 × 10\textsuperscript{−4} (8 × 10\textsuperscript{−5}) mbar. Following expansion, the molecular/cluster beam is skimmed (Beam Dynamics, 2 mm diameter orifice) as it enters the detection region. In this region, the ions are extracted orthogonally via pulsed voltage extraction into a mass spectrometer operated in linear time-of-flight mode.

IR photodissociation of M\textsuperscript{+}(\textsuperscript{+}CO\textsubscript{2})\textsubscript{n}−Ar complexes is performed using loosely focused tunable IR light generated from an OPO/OPA laser (LaserVision −10 Hz) with the IR beam overlapped with, and counterpropagating to, the cluster beam. The IR laser is calibrated using IR photoacoustic spectra of both CO and CO\textsubscript{2}. IR-REPD spectra are recorded by capturing mass spectra alternately with and without IR pulses for 150 laser shots at each wavelength. All spectra shown here were recorded in the range of the CO\textsubscript{2} asymmetric stretch (ν\textsubscript{as} = 2349 cm\textsuperscript{−1}), with all data acquisition and scanning controlled via a home-built LabVIEW routine.

Whenever the incident IR light is resonant with an IR-active mode of an Ar-tagged complex, IR photons can be absorbed and, following intramolecular vibrational relaxation (IVR), the Ar atom is lost from the complex. The result is depletion in the signal of the parent M\textsuperscript{+}(\textsuperscript{+}CO\textsubscript{2})\textsubscript{n}−Ar complex, which serves as a signature of photon absorption. Recording the depletion as a function of wavelength yields an infrared action spectrum of the complex.

To aid with assignment and interpretation, experimental spectra are compared with harmonic frequency calculations for a range of low-lying calculated cluster structures. Initial geometry optimization was performed on various starting geometries of the M\textsuperscript{+}(\textsuperscript{+}CO\textsubscript{2})\textsubscript{n} complexes generated via the stochastic KICK algorithm\textsuperscript{53} using the B3P86 density functional\textsuperscript{60} coupled with the Def2TZVP basis set\textsuperscript{67} on all atoms, without symmetric constraint. Singlet, triplet, and quintet spin states were considered for all complexes, with the triplet states found to be consistently lowest in energy for all complexes. This is expected for Co\textsuperscript{+} and Rh\textsuperscript{+}, which both have d\textsuperscript{5}F ground terms but is, perhaps, surprising for Ir\textsuperscript{+} given its 5d\textsuperscript{6}s\textsuperscript{5}F lowest energy term. Such effects have, however, been seen previously. A switching of the relative energetic ordering of different Fe\textsuperscript{+} electronic states upon complexation with CO\textsubscript{2} was observed by Armentrout et al.\textsuperscript{68} in their study of sequential bond energies in Fe\textsuperscript{+}(\textsuperscript{+}CO\textsubscript{2})\textsubscript{6}. In the present case the lower spin d\textsuperscript{5} configurations provide more symmetric structures than the d\textsuperscript{3}’s states in which hybridization is induced by incoming
ligands. All spectra have been recorded in the region of the CO$_2$ asymmetric stretch region and for this reason computational efforts were focused on M$^+$(CO$_2$)$_n$ complexes. We have not searched exhaustively for insertion, OM$^+$(CO$_2$)$_{n-1}$ complexes, but at least for $n > 2$, we found the M$^+$(CO$_2$)$_n$ complexes to be lower in energy.

Harmonic vibrational frequency calculations were performed on all unique structures identified to ensure they were indeed true minima (zero imaginary frequencies). Any found to possess higher symmetry were reoptimized within the highest possible symmetric point group. This ensures there are no significant differences between the symmetry-constrained and unconstrained energies and aids assignment of the electronic states and vibrational modes of each relevant structure. Additional calculations were performed on all unique structures in the presence of an Ar atom to determine any effect the rare gas tag may have. All calculations were performed using the Gaussian 09 suite of programs$^{49}$ and structural details for key structures are given in the Supporting Information accompanying this article. Lastly, simulated IR spectra of the unique structures of interest were generated by convoluting calculated IR signals with a Lorentzian line shape with full-width half-maximum (fwhm) of 4 cm$^{-1}$. Simulated IR spectra have been scaled (factor 0.962) such that the calculated asymmetric stretch region and for this reason computational efforts were focused on M$^+$(CO$_2$)$_n$ complexes. We have not searched exhaustively for insertion, OM$^+$(CO$_2$)$_{n-1}$ complexes, but at least for $n > 2$, we found the M$^+$(CO$_2$)$_n$ complexes to be lower in energy.

The Brucat group determined a dissociation energy,$^{26,31}$ whereas recent CCSD(T) investigations by Sodue et al. places this value at ca. 7450 cm$^{-1}$.$^{25}$ This is much greater than the photon energy in the vicinity of the asymmetric stretch of CO$_2$ (2349 cm$^{-1}$), thus necessitating the use of rare-gas tagging.$^{32,36}$ Even Ar binds strongly to Co$^+$. The Brucat group determined a Co$^+$(Ar) binding energy of 4111 cm$^{-1}$, and similar argon binding energies have previously been encountered in the case of Ni$^+(CO_2)_n$–Ar clusters studied by Duncan et al.$^{23}$ In the present case the result is that, even at high laser fluences, no photodissociation of the Co$^+$(CO$_2$)$_n$–Ar complex is observed.

Figure 3 shows the IR-REPD spectra recorded for the Co$^+$(CO$_2$)$_n$–Ar ($n = 2$–5) complexes in the region 2275–2450 cm$^{-1}$. The Co$^+$(CO$_2$)$_n$–Ar spectrum exhibits a single strong feature at 2385 cm$^{-1}$, i.e., blue-shifted ca. 36 cm$^{-1}$ from the frequency of the asymmetric stretch in free CO$_2$ (2349 cm$^{-1}$). Similar blue shifts have previously been observed in other M$^+$(CO$_2$)$_n$ complexes in the region 2275–2450 cm$^{-1}$.

For the $n = 2$ complex, both in-phase and out-of-phase combinations occur but, in the case of a linear (D$_{oo}$) complex, only the out-of-phase combination is IR-active. The single feature in the spectrum of Co$^+$(CO$_2$)$_2$–Ar is thus indicative of a linear, D$_{oo}$ configuration. Such a linear structure is consistent with the global minimum structure from DFT calculations (structure I, Figure 4). This is consistent with significant s–d hybridization with electron density directed away from the CO$_2$ ligands minimizing ion–ligand repulsion and encouraging ligand binding linearly on opposite sides of the metal cation.

III. RESULTS AND DISCUSSION

A. Co$^+$(CO$_2$)$_n$–Ar Spectra. Figure 2 shows the time-of-flight mass spectrum obtained via the laser ablation of a cobalt disk in the presence of a backing gas mixture of ca. 0.5% CO$_2$ in Ar. In addition to Co$^+$(CO$_2$)$_n$Ar and Co$^+$(CO$_2$)$_2$Ar$_2$ complexes, Co$^+$(CO$_2$)$_n$ (×) and Co$^+$(CO$_2$)$_n$Ar$_2$ (†) complexes are formed. Qualitatively similar time-of-flight spectra are obtained following ablation of rhodium and iridium targets.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** IR-REPD spectra for the Co$^+$(CO$_2$)$_n$–Ar complexes recorded in depletion of the parent ion signal in the region of the CO$_2$ asymmetric stretch. The IR-REPD spectrum for the untagged Co$^+$(CO$_2$)$_4$ complex is also included for comparison. The vertical dashed line indicates the vibrational frequency of the asymmetric stretch ($\nu_3$) of free CO$_2$ at 2349 cm$^{-1}$.
This rationale also accounts for the linear structure calculated for the Sr+(CO2) complex.52

As the number of CO2 ligands increases, an additional vibrational band appears in the IR spectra to the red of the original band (Figure 3). This new band gradually red-shifts with increasing n toward the free CO2 value at 2349 cm−1. For the Co+(CO2)3 complex, multiple vibrational modes arise. A planar D3h structure would have a single IR-active mode and can thus be ruled out. Our DFT calculations suggest a global minimum structure with a near-linear Co+(CO2)2 “core” structure (Figure 4, structure I) and a third CO2 weakly bound in a nonplanar structure (structure II, Figure 4; see also Supporting Information). The spectral signature of the weakly bound CO2 is still blue-shifted from free CO2 (by ca. 20 cm−1). The relative binding energies of the third is borne out in the calculated M+(CO2)n complexes,19,22,23 in agreement with predictions. Other spin multiplicities have been considered but, in each case, triplet state structures which agree well with the experimental spectrum. Including an argon atom in the calculations does not significantly affect the relative energies of the two isomers. Other spin multiplicities have been considered but, in each case, triplet state structures are consistently the lowest in energy. Bent geometries similar to that of structure IV have been observed previously for the Al+(CO2)2 complexes.16,17

B. Rh+(CO2)n−Ar Spectra. The IR-REPD spectra for the Rh+(CO2)n−Ar complexes are presented in Figure 5. In contrast to the Co+(CO2)2−Ar, spectrum, the Rh+(CO2)2−Ar spectrum shows two peaks (at ca. 2401 and 2373 cm−1) blue-shifted by 52 and 24 cm−1, respectively, from the free CO2 stretch. This is consistent with in-phase and out-of-phase linear combinations of CO2 stretches indicating a nonlinear structure. Our calculations predict a near-linear, C2v structure as the global minimum (structure III, Figure 6), but this is inconsistent with the experimental spectrum as it predicts only a single IR band in this region. At least one other isomer must be present.

We calculate a low-lying C2v symmetry with an O2C=O bond angle of 109.3° (structure IV, Figure 6) around 0.21 Å, 2.16 Å for the third CO2 (for structural details, see the Supporting Information). The relative binding energies of successive ligands also reflects this structure with a halving of the Co+(CO2)n−1−CO2 binding energy between n = 2 and 3 (from ca. 0.91 to 0.43 eV; vide infra).

A coordination number of 2 for a gas-phase M+(CO2)n complex is not unprecedented. Both Al+(CO2)2 and Si+(CO2)2 show an increase in photodissociation yield for n > 2.17,18 Larger coordination numbers, however, are more common, as in the case of V+, Ni+, and Fe+( n ≥ 4).19,22,23 In Co+(CO2)n, the spectrally observed trend is, however, established by n = 3. With increasing n > 3, two bands are observed, one close to 2385 cm−1 consistent with the Co+(CO2)2 core, and a second, whose blue shift decreases with increasing n, due to more weakly bound ligands. It is also notable that the relative intensity of the latter band increases relative to that of the 2385 cm−1 band as the number of ligands attached increases.

Figure 4 also shows the IR-REPD spectrum for the non-Ar-tagged Co+(CO2)14 complex shown as a typical example of the spectra of the larger clusters. These are all very similar in showing a broad feature close to the free CO2 stretch (possibly unresolved multiple shell structure) and a “core” band whose blue shift is slightly larger than for the very smallest complexes, possibly reflecting increased rigidity in larger coordination shells where ligand–ligand interactions are more important. The presence of these intermediate shells has previously been inferred in the spectra of cationic Fe+, Ni+, and V+(CO2)n complexes.19,22,23

Figure 5 shows the DFT calculated vertical IR-REPD spectra for the Rh+(CO2)n−Ar complexes. The experimental spectrum as it predicts only a single IR band in this region. At least one other isomer must be present. The origin of nonlinearity of ML2 molecules has received considerable computational attention in the context of...
As for the Co*(CO2)3−Ar complex, the new feature may be understood in terms of a CO2 weakly bound to the nonlinear Rh*(CO2)2 core. This is supported by DFT with the simulated IR spectrum calculated to be significantly more polarizable than the Co* ion (α = 20.6. a0^3), which would support a more bent structure for Rh*(CO2)2 than for Co*(CO2)2.

The Rh*(CO2)2−Ar IR-REPD spectrum shows three clear bands—the same two observed for the n = 2 complex plus a strong new band, at 2364 cm−1, closer to the free CO2 stretch. As for the Co*(CO2)−Ar complex, the new feature may be understood in terms of a CO2 weakly bound to the nonlinear Rh*(CO2)2 core. This is supported by DFT with the simulated IR spectrum of the lowest energy structure (structure V, Figure 6) showing three such bands (albeit with relative intensities differing from the experimental spectrum). Again, the M*−ligand bond lengths are markedly shorter for the “core” CO2 ligands (ca. 2.20 Å), than for the more weakly bound CO2 ligand (2.35 Å, see the Supporting Information).

As the number of ligands increases, so the vibrational mode due to weakly−bound CO2 molecules tends further toward the free CO2 band (Figure 5), reflecting the fact that each successive additional ligand that binds to the Rh*(CO2)2 “core” experiences weaker perturbation. Beyond n = 6, the most blue−shifted band (interpreted as the in-phase combination of the CO2 asymmetric stretch in the core Rh*(CO2)2 cluster) becomes too weak to be observed. This may result from the core becoming increasingly linear as the number of ligands increases, rendering this mode IR-inactive. The IR-REPD spectra of the larger n > 6 complexes can thus be interpreted as a single core vibrational mode (around 2385 cm−1) and an intense, unresolved feature around the wavenumber of free CO2 reflecting the outer ligands.

C. Ir*(CO2)3−Ar Spectra. Figure 7 shows the IR-REPD spectra for the Ir*(CO2)3−Ar complexes. The smallest complex (n = 2) exhibits one strong feature that appears at ca. 2367 cm−1 accompanied by a broader shoulder that extends to 2400 cm−1. The similarity with the spectrum of Rh*(CO2)2−Ar indicates a nonlinear structure of Ir*(CO2)3.

Calculations predict a C_{2h} global minimum structure (Figure 8, structure VI) for Ir*(CO2)3, but a C_{2v} isomer (structure VII) some 0.79 eV higher in energy provides a better match with the experimental spectrum. In this case, the presence of the Ar tag changes the relative energetic ordering of low-lying structures with the C_{2v} variant of Ir*(CO2)3−Ar calculated to be the global minimum (structure VIIa). This structure is not unlike the lowest energy structure calculated for Rh*(CO2)2 (structure IV, Figure 6).

The polarizability of Ir* (α = 27.9 a0^3; ref 54) is intermediate between that of Co* and Rh*, and this is reflected in Ir*−O bond lengths of 2.06 Å (2.03 Å) for structure VI (VII), which lie between the 1.95 Å in Co*(CO2)2 and 2.15 Å (2.23 Å) in Rh*(CO2)2 for structure III (IV).

The spectrum of the n = 3 complex (Figures 7 and 9) shows three clearly resolved bands with one band, at 2350 cm−1, very close to free CO2 stretch. This indicates a very weakly interacting ligand consistent with a secondary solvent sphere. Again, DFT calculations support this idea, with the lowest energy structure comprising a nonlinear Ir*(CO2)3 “core” (with M*−O bond lengths 2.07 Å (ca. 2.07 Å)) with the third CO2 ligand bound somewhat further away (M*−O distance 2.57 Å (2.48 Å), structure VIII (IX), Figure 9). The simulated IR spectra of the two lowest energy structures (including the

Figure 6. Experimental IR-REPD spectra for the Rh*(CO2)2−Ar and Rh*(CO2)14−Ar complexes shown together with the simulated IR spectra for energetically low-lying candidate structures calculated at the B3P86/Def2TZVP level of theory. By convention, all energies are specified relative to the energy of the putative global minimum structure.

Figure 7. IR-REPD spectra for the Ir*(CO2)3−Ar complexes recorded in depletion of the parent ion between 2275 and 2450 cm−1. The IR-REPD spectrum for the untagged Ir*(CO2)14 complex is also included for comparison. The vertical dashed line indicates the vibrational frequency of the asymmetric stretch (ν3) of free CO2 at 2349 cm−1.

Figure 8. IR-REPD spectra for the Ir*(CO2)3−Ar complexes shown together with the simulated IR spectra for energetically low-lying candidate structures calculated at the B3P86/Def2TZVP level of theory. By convention, all energies are calculated relative to the energy of the putative global minimum structure.
The respective Ar-tagged counterparts compare well with the experimental IR-REPD spectrum. The Ir\(^+(\text{CO}_2)\)_n−Ar complexes show more structured IR-REPD spectra than the Co\(^+(\text{CO}_2)\)_n and Rh\(^+(\text{CO}_2)\)_n complexes, the wavenumber of the feature associated with the “core” (ca. 2365 cm\(^{-1}\)) initially red-shifts with the sequential addition of another two CO\(_2\) ligands, appearing at ca. 2353 cm\(^{-1}\) for the \(n = 5\) complex. From \(n = 6\) onward, however, this feature subsequently blue-shifts as further CO\(_2\) ligands are attached, reaching ca. 2365 cm\(^{-1}\) for the Ir\(^+(\text{CO}_2)_{15}\) complex. It is likely that \(n = 6\) represents a full secondary solvation shell, with an Ir\(^+(\text{CO}_2)\)_2 core and four more weakly bound ligands, lending a degree of rigidity to the complex structure. This idea is supported by the fact that the in-phase asymmetric stretching combination of the Ir\(^+(\text{CO}_2)\)_2 “core” follows the same trend as the out-of-phase asymmetric stretching combination.

D. Trends and Comparisons. Figure 10 shows a summary of the trends in the vibrational bands identified for all species observed in this study as a function of increasing number of ligands. All spectra for \(n \leq 10\) were recorded with Ar-tagging, those for \(n > 10\) without. The Co\(^+(\text{CO}_2)\)_n spectra are anomalously simple in exhibiting a single vibrational band for the \(n = 2\) complex reflecting the higher symmetry of the Co\(^+(\text{CO}_2)\)_2 “core”. All bands show a progressive red shift (i.e., toward the free CO\(_2\) band) as \(n\) increases 2–5 by which time, in the case of the Rh\(^+\) and Ir\(^+\) complexes, one vibrational mode (assigned to vibrations in noncore ligands) has reached the free CO\(_2\) wavenumber. Beyond \(n = 5\), the higher wavenumber bands blue-shift further and do not appear to have reached their asymptote by \(n = 15\) (the largest cluster studied here).

The DFT simulations suggest that all three systems studied exhibit a “core” M\(^+(\text{CO}_2)\)_2 structure to which additional ligands bind more weakly. This is supported by the trend in binding energy as a function of CO\(_2\) ligands, displayed in Figure 11, which shows that the third CO\(_2\) ligand binds much more weakly than the first two in all three sets of M\(^+(\text{CO}_2)\)_n complexes. Additionally, the geometrical structures of the M\(^+(\text{CO}_2)\)_2 complexes are different, with the bond angle apparently correlated with the polarizability of the metal ion. The weakly polarizable Co\(^+\) (\(\alpha = 20.6\ a_0^3\)) results experimentally in a linear Co\(^+(\text{CO}_2)\)_2 structure, which exhibits a single vibrational band in its IR-REPD spectrum. The much higher polarizability of Rh\(^+\) (\(\alpha = 34.4\ a_0^3\)) leads to the formation of a very bent, low-lying Rh\(^+(\text{CO}_2)\)_2 isomer, which results in two clear vibrational bands being observed. Lastly, Ir\(^+(\text{CO}_2)\)_2 has an intermediate, weakly bent, structure reflecting the Ir\(^+\) polarizability of 27.9\ a_0^3. All of these structures distort upon addition of further ligands but their signature remains in markedly shorter bond lengths for two CO\(_2\) molecules.

IV. CONCLUSIONS

A combination of infrared resonance-enhanced photodissociation spectroscopy and density functional theory has been applied to investigate the structures of gas-phase M\(^+(\text{CO}_2)\)_n (M = Co, Rh, Ir; \(n = 2−15\)) ion–molecule complexes. The results yield new details on the key interactions between metal ions
untagged M+(CO2) indicate Ar-tagged complexes and triangular markers the larger, to determine the position of a particular peak. The square markers indicate M+(CO2) complexes. The uncertainties in the peak positions correspond to the full-width-half-maximum (fwhm) of a fitted Gaussian function employed to determine the position of a particular peak. The square markers indicate Ar-tagged complexes and triangular markers the larger, untagged M+(CO2) complexes. The horizontal dashed line marks the vibrational frequency of the asymmetric stretch (ν3) of the free CO2 molecule at 2349 cm⁻¹.

Figure 10. Experimental peak positions displayed as a function of cluster size for the M+(CO2)n complexes (n = 2–15, M = Co, Rh, and Ir). The uncertainties in the peak positions correspond to the full-width-half-maximum (fwhm) of a fitted Gaussian function employed to determine the position of a particular peak. The square markers indicate Ar-tagged complexes and triangular markers the larger, untagged M+(CO2) complexes. The horizontal dashed line marks the vibrational frequency of the asymmetric stretch (ν3) of the free CO2 molecule at 2349 cm⁻¹.

Figure 11. Calculated binding energies of successive CO2 ligands to M+(CO2)₃ complexes (M = Co, Rh, and Ir) complexes. The binding energies are determined by calculating the energy difference between putative global minima of the parent complex and the pertinent products from CO2 loss.

and CO2 ligands. In particular, these studies highlight the central role played by a tightly bound core of M+(CO2)₂ to which subsequent ligands bind less tightly. The evidence for this comes both from experiment (relative blue-shifted frequencies of different ligands) and from calculation of successive ligand binding energies.

ASSOCIATED CONTENT
3 Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.6b10902.

Energies and structural parameters for calculated low energy structures (PDF)

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
A.S.G. is grateful to the EPSRC for funding his postdoctoral position. A.K. is grateful to the Royal Society for his Newton Fellowship. A.L is grateful to Wadham College and EPSRC for his graduate studentship. The authors are grateful to Advanced Research Computing facility at the University of Oxford for providing supercomputer facilities. This work is funded by EPSRC under Programme Grant EP/L005913/1.

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Spectroscopy of Na+(CH3OH)2  
−  
Complex: Making and Breaking the Inter-Water Hydrogen-Bond.  
Spectroscopy of Na+(CH3OH)2  
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Mg+(CO2)6  
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