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IR Spectroscopy of M$^+$(Acetone) Complexes (M = Mg, Al, Ca): Cation−Carbonyl Binding Interactions

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

Introduction

Gas-phase metal ion complexes provide models for metal−ligand interactions,[1−4] metal ion solvation,[3−5] and the binding of cations in biological systems.[6−9] In the latter case, cation binding to proteins often takes place at the carbonyl groups of component amino acids.[6−11] Vibrational spectroscopy can provide insight into the cation binding site and condition, but in proteins the carbonyl, or so-called "amide I," region of infrared spectra is often overlapped by absorptions from other functional groups.[10,11] In the present study, we isolate and investigate the cation−carbonyl interaction in detail with model cation−acetone complexes of magnesium, aluminum, and calcium. Infrared spectroscopy in the carbonyl stretch region reveals the effect of cation binding for different metals, and comparison to theory provides the structures of these complexes.

Metal ion complexes of magnesium, aluminum, and calcium have been studied previously with various forms of mass spectrometry.[12−20] Collision-induced dissociation,[20] and other related methods, have been employed to obtain the dissociation energies for these complexes. Electronic spectroscopy measurements have been productive for Mg$^+$ and Ca$^+$ complexes because of the convenient atomic transitions of the alkaline earth cations at low energies.[21−27] Mg$^+$(acetone) photodissociation has been studied at 355 nm.[23] Aluminum complexes have less convenient electronic absorptions,[28] but their low ionization energies[29,30] have made it possible to perform ZEKE or MATI photoelectron spectroscopy[30,31] on these systems. Newer studies have applied infrared photodissociation spectroscopy to complexes of these metal cations with ligands such as CO_2, H_2O, CH_3OH, and NH_3.[32−36] In related work, Lisy and co-workers have studied the infrared spectroscopy of alkali cation−acetone complexes in the C−H stretching region.[37] Ab initio calculations have investigated the energetics of bonding and the structures of these metal ion−molecule complexes.[24,25,32,35,36,38−46]

Although IR spectroscopy provides much information about the structure of cation−molecular complexes, its applications have been limited because the required tunable IR lasers are not generally available. Previous studies have employed tunable IR optical parametric oscillators (OPOs) in the higher frequency region of the spectrum (2000−4000 cm^{-1}),[32−37] whereas the lower frequency region was only covered by free-electron lasers (FELs). Using FELs, new work has studied amino acid or peptide ions and some examples of their metal cation complexes.[47,48] In recent technology developments, the capability of OPOs has been extended to the frequency region below 2000 cm^{-1} with new $AgGaSe_2$ crystals.[49] Johnson and co-workers have employed this technology recently to study hydroxide−water anions and protonated water clusters.[50] In the present work, we use this latter methodology for the first time for metal cation−molecular complexes. In a study of cation−acetone complexes, we probe the carbonyl stretch region near 1700 cm^{-1}. In coordination with theoretical calculations, we investigate the structures and bonding interactions in these systems.

Experimental Section

Metal ion complexes with acetone are produced by pulsed laser vaporization (355 nm; Nd:YAG) of the respective metal rod samples mounted in a rotating rod, pulsed nozzle source.[4,34] Acetone is added to the argon expansion gas at ambient pressure, and cation clusters of the form M$^+$(acetone)$_n$Ar$_m$ are produced for $n = 1-10$ and $m = 1, 2$. These complexes are detected and mass-selected with a reflectron time-of-flight mass spectrometer, as described previously.[4,34] Tunable infrared radiation is produced with a specially designed infrared optical parametric oscillator/amplifier (OPO/OPA) system (LaserVision). A Nd:YAG laser at 532 nm pumps the oscillator section of this

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TABLE 1: Binding Energies of Complexes Relevant for This Study

complex	energy (kcal/mol) theory	energy (kcal/mol) experimental
Mg^+(acetone)	41.3[a] 45.6[c]	41.4[b]
Al^+(acetone)	41.5[d] 42.7[c]	
Ca^+(acetone)	41.0[c]	
$MgAr^+$		3.70 (1295 cm^{-1})[e]
$AlAr^+$		2.81 (982.3 cm^{-1})[f]
$CaAr^+$		2.00 (700 cm^{-1})[g]

[a] Reference 46. [b] Reference 20 g. [c] This work. [d] Reference 38b. [e] Reference 21g. [f] Reference 29. [g] Reference 22b.

system, which employs two KTP crystals. The signal beam in the 900 nm (11 100 cm^{-1}) region is then combined with the residual Nd:YAG fundamental frequency (1064 nm; 9400 cm^{-1}) in a $AgGaSe_2$ crystal (7 × 7 × 25 mm; 50° cut). Difference frequency generation produces the desired output near 1700 cm^{-1} with an energy of about 200 μJ/pulse. This crystal provides useful IR over the range of about 800 to 1850 cm^{-1}. We performed scans here for all three complexes in the region of 1550 to 1850 cm^{-1}, where the carbonyl stretch resonances are expected.

Density functional theory (DFT) calculations (Gaussian 03W)[51] were carried out at the B3LYP level[52] using the 6-311+G** basis set on the M^+(acetone) and M^+(acetone)Ar complexes. Vibrational scaling factors in the range of 0.96−1.00 were investigated to determine the best value appropriate for these metal cation−carbonyl complexes.

Results and Discussion

The laser vaporization method produces copious quantities of $M^+(\text{acetone})_n$ complexes as well as those tagged with one or more argon atoms. The M^+-(acetone) binding energy has been determined previously by experiment and theory for these metals.[20g,38b,46] As shown in Table 1, these values are in excess of 40 kcal/mol (14 000 cm^{-1}). Therefore, infrared excitation at the fundamental frequency of the carbonyl stretching vibration near 1700 cm^{-1} does not have enough energy to break these bonds. To achieve more efficient photodissociation in these systems, we employ the method of rare gas atom tagging with argon.[32−36,50,53−56] As also shown in Table 1, the binding energy of argon to the metal cations here is rather low. In every case the known binding in the M^+−Ar diatomic molecules is much less than 1700 cm^{-1}, and therefore we expect that the argon binding in the M^+(acetone)Ar mixed complexes will also be less than this infrared excitation energy. We find in practice that all three M^+(acetone)Ar complexes dissociate efficiently with infrared excitation by eliminating the argon atom.

Figure 1 shows the infrared photodissociation spectra of the three M^+(acetone)Ar complexes, measured in the argon-loss mass channel. As shown, all three systems exhibit resonances in the 1700 cm^{-1} region. No other resonances were found in the range scanned (1550 to 1850 cm^{-1}). The carbonyl stretch in the free acetone molecule occurs at 1731 cm^{-1},[57] which is indicated with the vertical blue dashed line. As shown, the resonances in the cation−acetone complexes all occur at frequencies lower than this free-molecule value. The dissociation yield is greater for the Mg^+ and Al^+ complexes than it is for the Ca^+ complex, and this accounts for the different relative signal/noise levels in these spectra. The Mg^+ and Ca^+ complexes have two bands in this region, whereas the Al^+ complex has only one. However, the Al^+ complex band is shifted much more to the red than the bands in the Mg^+ and Ca^+ spectra. The strong shift of the carbonyl stretch is consistent with metal ion binding on the carbonyl of acetone, as we would expect from electrostatic considerations. To interpret these spectra in more detail, we consider the causes of the red-shifted bands and the doublet structure that occurs for the Mg^+ and Ca^+ complexes.

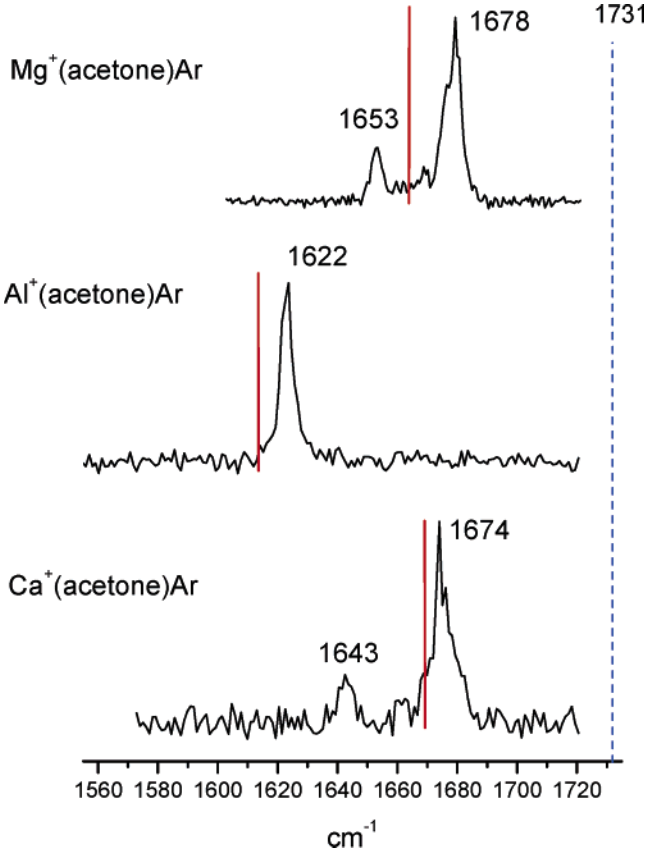


Figure 1. Infrared photodissociation spectra of Mg^+, Al^+, and Ca^+ complexes with acetone in the carbonyl stretching region. The argon-tagged complex was mass-selected, and the argon elimination mass channel was recorded. The red bars show the predicted C═O stretch frequency from density functional theory calculations using a vibrational scaling factor of 0.990.

The vibrational frequencies of molecular ligands are often found to shift to lower frequencies compared to those same vibrations in the corresponding free molecules upon binding with a metal. In conventional inorganic and organometallic chemistry, this is seen commonly for metal−carbonyl complexes.[58] We have reported similar trends for isolated gas-phase species, where the ligand was acetylene,[59] benzene,[60] water,[61] or nitrogen.[62] In all of these systems, the cation binding withdraws bonding electron density from the highest occupied molecular orbitals of the ligand in the region of the cation attachment site via so-called σ-type donation. For transition metals, π-type back-bonding may also be present, which pushes d-electron density into low-lying ligand antibonding orbitals, and this can also weaken the ligand bonding. However, in the present systems there are no partially filled d orbitals, and σ-donation is the main basis for charge transfer. If these metal ions bind on the carbonyl of acetone, then the orientation is different from conventional metal−carbonyl complexes, but the mechanism of charge transfer should be similar. The highest occupied molecular orbital of acetone is the nominally nonbonding b_2 orbital containing the oxygen lone-pair electrons, but this orbital also has partial bonding character, and the next lowest π-bonding b_1 orbital has density in this same spatial

TABLE 2: Energetics and Selected Vibrational Frequencies Calculated with Density Functional Theory for These Metal Ion−Acetone Complexes[a]

complex	M$^+$−L binding energy (D$_e$; kcal/mol)	vibrational frequencies (cm^{-1})	
Mg$^+$(acetone)	45.6	M$^+$−L stretch	309
		sym C−C−C stretch	839
		C═O stretch	1680 (1663)
Al$^+$(acetone)	42.7	M$^+$−L stretch	283
		sym C−C−C stretch	842
		C═O stretch	1630 (1614)
Ca$^+$(acetone)	41.0	M$^+$−L stretch	255
		sym C−C−C stretch	831
		C═O stretch	1686 (1669)

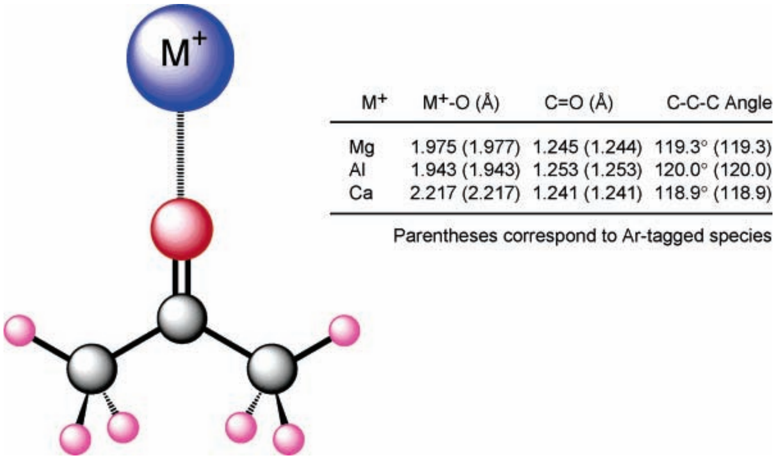
[a] The C═O frequencies in parentheses are those resulting from scaling with a factor of 0.990.

region. Binding on the oxygen end of the acetone carbonyl can polarize both of these orbitals. Therefore, it is understandable that metal ion binding on the carbonyl of acetone withdraws bonding electron density and this lowers the frequency of the carbonyl stretching vibration.

To be more quantitative about these vibrational shifts, we have investigated each of these complexes with density functional theory (DFT) calculations. We have studied both the neat M$^+$(acetone) complexes as well as those tagged with argon. This data is summarized in Table 2, and a full account of these calculations is provided in the Supporting Information. We find lowest energy structures for all complexes that have the metal cation binding on the oxygen atom, maintaining the overall C_{2v} symmetry of the complex, as shown in Figure 2. Although dissociation energies calculated with DFT are not expected to be quantitative, the complex binding energies follow the trend Mg$^+$ > Al$^+$ > Ca$^+$. In the case of the Mg$^+$ complex, our binding energy is comparable to but slightly higher than that calculated previously,[46] and it is in reasonable agreement with available experiments.[20b] The argon complexes each bind the rare gas atom on the metal ion. There are only slight energy differences between configurations with the rare gas on the C_2 axis in a linear O−M$^+$−Ar configuration, as opposed to a bridging structure with it interacting with both the metal ion and a C−H hydrogen. For Mg$^+$ and Al$^+$, the argon bridging configurations are preferred, whereas Ca$^+$ prefers the linear O−M$^+$−Ar configuration. We have discussed the tendency of Mg$^+$ and Al$^+$ to form such bent di-ligand configurations in our previous work.[31−35] The DFT frequencies of the acetone-based vibrations in all three complexes are virtually unchanged (shifts of 1−2 cm^{-1}) by the addition of the argon, regardless of its position. The carbonyl stretch frequency calculated for each complex is shown in Figure 1 as a vertical red bar. As indicated, DFT predicts that the carbonyl stretch undergoes a red shift upon binding to each of these metal cations. The relative amount of the red shift calculated (greater for the aluminum complex) is also consistent with the experiment. However, the quantitative positions of the vibrational bands calculated depends on the vibrational scaling factor applied, as discussed below.

As usual, the harmonic vibrational frequencies derived from DFT are expected to be higher than the true anharmonic vibrations in these molecules, and it is typical to apply a scaling factor to account for this. If we compare a DFT calculation for the free-acetone carbonyl stretch to the experimental value for this vibration, then we derive a scaling factor of 0.969. However, application of this scaling for the metal ion complexes here leads to an exaggerated prediction for the red shift of the carbonyl vibration in all three systems. This leads to theoretical frequencies that lie 20−45 cm^{-1} lower than the experimental values. This is surprising because DFT frequencies scaled like this have led to almost perfect agreement with vibrational spectra that we have measured previously for other ligands in higher frequency regions of the spectrum.[32−35,59−62] However, it is well-known that scaling factors become closer to unity as the frequencies of vibrations become lower and scaling derived from organic ligands may not work well for inorganic complexes.[63] Because so few systems similar to these have been studied in the past, it is not clear what scaling factor is appropriate to use here. We therefore present the unscaled values for the carbonyl stretch frequencies here in our Supporting Information. We then experimented with different trial values for the scaling factor to investigate the appropriate value to use for these systems. We find that a value of 0.990 leads to good agreement between experiment and theory for all three complexes. This value is shown with the red bars in Figure 1. This same problem of carbonyl scaling factors has been recognized already in the one previous IR study of catonized amino acid and peptide ions.[47c]

Theory also helps us to understand the doublet features observed here for the magnesium and calcium complexes. As shown in the Figure, only one IR band is expected for each carbonyl resonance. We explored different binding configurations for the metal ion interacting with acetone and with argon, but in each case only one structure is found to lie at low energy. This effectively rules out different isomeric structures as the source of the multiplet bands. We also considered the possibility of the presence of both enol- and keto-tautamers as a source of



M$^+$	M$^+$-O (Å)	C=O (Å)	C-C-C Angle
Mg	1.975 (1.977)	1.245 (1.244)	119.3° (119.3)
Al	1.943 (1.943)	1.253 (1.253)	120.0° (120.0)
Ca	2.217 (2.217)	1.241 (1.241)	118.9° (118.9)

Parentheses correspond to Ar-tagged species

Figure 2. Structures calculated with density functional theory for the three acetone complexes. The structural parameters for each metal are given in the table.

isomeric structures, but for all of these complexes our DFT calculations show that the enol species lies at much higher energies than the keto form and is thus not likely to be present. A final possibility for multiplet structure near the carbonyl stretch is a Fermi resonance. Table 2 shows the frequencies calculated for other relevant vibrations of these complexes. Fermi resonance may occur whenever there is an accidental near-degeneracy of any two (or more) vibrational states having the same frequency. In this particular system, a_1 vibrational states that can couple with the carbonyl stretch may result from fundamentals or combinations of a_1 modes or overtones of any modes regardless of their symmetry. Of particular interest here, the symmetric C−C−C carbon stretch has the same a_1 symmetry as the carbonyl stretch, and the overtone of this mode is almost exactly degenerate (within about 20 cm^{-1}) of the carbonyl stretch for the Mg^+ and Ca^+ complexes. In the case of the aluminum complex (where the carbonyl is much more red-shifted) this combination is not nearly as close (the C=O stretch vibration is more than 50 cm^{-1} lower than the carbon stretch overtone). We therefore assign the multiplet structure seen for the Mg^+ and Ca^+ complexes but not for Al^+ to such a Fermi resonance between the carbonyl stretch and the symmetric carbon stretch overtone. To confirm this possibility, we measured the spectrum for the Mg^+ complex with ^{13}C isotopically substituted at the carbonyl carbon (see the Supporting Information). In this complex, a doublet is seen again, but *both* members are shifted to the red compared to their positions in the unsubstituted species, and their relative intensities are changed. This behavior is consistent with a Fermi resonance, confirming this as the most likely assignment for the doublets. We can therefore take the average values of the doublets seen for the Mg^+ and Ca^+ complexes as approximate measures of the actual carbonyl stretch frequencies.

It is clear from both the experiment and theory that the Al^+ ion induces a much greater shift on the carbonyl stretch of acetone than either Mg^+ or Ca^+. As noted above, the red shift of this vibration is associated with a charge-transfer effect caused by the cation polarizing the lone pair and bonding electrons on the carbonyl. The electrostatics of such a charge induction are favored when the charge is “focused” into a small volume so that it more closely resembles a point charge. With its closed-shell configuration, Al^+ ($3s^2$) has a smaller ionic radius (72 pm) than either Mg^+ (82 pm) or Ca^+ (118 pm),[64] both of which have ns^1 open-shell configurations. Consistent with this smaller size, the Al^+ complex has the shortest M^+−O bond distance of these three complexes. With its smaller size and closer approach to the carbonyl, it is then understandable that the polarization of the carbonyl is greatest for Al^+. Interestingly, although the vibrational shift is greatest for Al^+, this complex is apparently not the most strongly bound of these three. The vibrational shifts and the dissociation energies therefore do not follow the same trend. We have found this same effect previously in a series of transition metal ion complexes with acetylene.[59a] Focusing on this same issue, Frenking and co-workers have decomposed the various contributions to metal−ligand bonding and have explained that vibrational shifts depend on the strength of the interaction but also on the details of the M^+−L separation and the specific orbital interactions involved in the bonding.[58] Future studies will explore the carbonyl stretch in acetone or other related systems with a variety of metal ions to further investigate the details of these interactions.

Conclusions

Metal cation complexes (M = Mg, Al, Ca) are produced in a cold molecular beam environment and studied with infrared photodissociation spectroscopy in the carbonyl stretch region. These experiments are made possible by the availability of new OPO laser systems in the longer wavelength region of the IR. The structures and spectra of these complexes are also investigated with density functional theory. The spectroscopy and theory are consistent with structures having the metal cation binding on the oxygen of the carbonyl for all three complexes. The carbonyl stretch vibration in each of these complexes shifts to lower frequency compared to its value in the free acetone molecule. This affect is attributed to a charge-transfer interaction because the metal cation withdraws bonding electron density from the carbonyl. The effect is greatest for the closed-shell aluminum cation because of its smaller size and greater charge density, which enhances its ability to induce polarization of the carbonyl electrons. A Fermi resonance between the carbonyl stretch and the overtone of the symmetric carbon stretch vibration leads to a doublet structure at the carbonyl band for Mg^+ and Ca^+ complexes. However, this accidental degeneracy is not found for the Al^+ complex because the carbonyl stretch occurs at a much lower frequency. The qualitative trends in the carbonyl stretch vibration are reproduced nicely by theory, but the absolute values of the vibrational frequencies are sensitive to the scaling factors employed. We find that the best overall agreement between theory and experiment in these simple model systems occurs when a vibrational scaling factor of 0.990 is employed.

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

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Supporting Information Available: Full results for DFT calculations for all of the isomeric and tautomeric structures considered and the spectrum of the isotopically substituted (^{13}C) Mg^+(acetone) complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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