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Vibrational Spectroscopy of $Ni^+(benzene)_n$ Complexes in the Gas Phase

T. D. Jaeger and M. A. Duncan*

Department of Chemistry, University of Georgia, Athens, Georgia 30602-2556

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$Ni^+(benzene)_n$ ($n = 1-6$) and $Ni^+(benzene)_nAr_{1,2}$ ($n = 1,2$) are produced by laser vaporization in a pulsed nozzle cluster source. The clusters are mass selected and studied by infrared laser photodissociation spectroscopy in a reflectron time-of-flight mass spectrometer. The excitation laser is an OPO/OPA system that produces tunable IR in the C−H stretching region of benzene. Photodissociation of $Ni^+(benzene)_n$ complexes occurs by the elimination of intact neutral benzene molecules, while $Ni^+(benzene)_nAr_{1,2}$ complexes lose Ar. This process is enhanced on resonances, and the vibrational spectrum is obtained by monitoring the fragment yield versus the infrared wavelength. Vibrational bands in the 2700−3300 cm^{-1} region are characteristic of the benzene molecular moiety with systematic shifts caused by the metal bonding. A dramatic change in the IR spectrum is seen at $n = 3$ and is attributed to the presence of external benzene molecules acting as solvent molecules in the cluster. The results of previous theoretical calculations are employed to investigate the structures, energetics, and vibrational frequencies of these complexes. The mono-benzene complex is found to have a C_{2v} structure, with benzene distorted by the metal π-bonding. The di-benzene complex is found to have a D_{2h} structure, with both benzenes distorted. The comparison between experiment and theory provides intriguing new insight into the bonding in these prototypical π-bonded organometallic complexes.

Introduction

Transition-metal ion−molecule complexes that are produced, isolated, and studied in the gas phase provide models for metal−ligand interactions and metal ion solvation.[1−4] Metal ion−benzene complexes are of particular interest for their relevance to catalytic and biological processes.[5,6] Such π-bonded systems are prevalent throughout organometallic chemistry.[7,8] Metal ion−benzene complexes are also fascinating because they form sandwich structures.[7,8] These systems can be compared to similar complexes that are synthesized and isolated using conventional techniques.[7,8] Condensed phase complexes have been studied using infrared and Raman spectroscopy, and shifts in the ligand-based vibrations give information on the metal−ligand interaction.[9−12] Gas-phase ion studies of vibrational spectroscopy are highly problematic because of the low densities of ion−molecule species that can be produced. However, we and others have demonstrated that IR spectroscopy can be measured for these complexes using photodissociation spectroscopy with new kinds of infrared lasers.[13−16] In the present report, we apply these methods to $Ni^+(benzene)_n$ complexes.

Interest in organometallic sandwich complexes began with the discovery of ferrocene and the explanation of its bonding stability due to metal−ligand charge-transfer and the familiar 18-electron rule.[17] Shortly after that work, the closely related dibenzene chromium complex was synthesized and isolated.[9] Several other neutral metal−benzene analogues have been isolated and studied via these conventional techniques in condensed phases, as have other complexes that carry a net charge and are stabilized via counterions.[7,8] Infrared and Raman spectroscopy has been applied to these complexes to investigate their structures.[9−12] Although qualitative trends of shifts in the ligand based modes were established, many uncertainties arose from solvent effects and the presence of counterions. It is therefore interesting to study metal ion−benzene complexes in the gas phase where such effects are absent.

Many metal ion−benzene complexes have been studied in the gas phase by mass spectrometry.[18−23] Bond energies have been determined using collision-induced dissociation (CID),[20] equilibrium mass spectrometry,[21] and UV−vis photodissociation.[18,19] Theory has investigated the structures and energetics of these systems.[2,3,24−30] Kaya and co-workers demonstrated that various metal−benzene complexes form multiple-decker sandwich structures with alternating layers of ligands and metal, while other metal−benzene systems seemed to form so-called "rice-ball" structures with metal cluster cores surrounded by ligands.[22] The tendency to form multiple-decker sandwiches is most pronounced for early transition metals, such as vanadium or titanium, while later transition metals are more likely to form rice-ball geometries. The multiple-decker sandwich structures were confirmed by Bowers and co-workers using ion mobility measurements,[23] as well as by recent magnetic deflection experiments by Kaya and co-workers.[22f] Photoelectron spectroscopy has been applied to metal−benzene anions.[22b,31] Recently, an IR absorption spectrum was obtained for V^+-(benzene)$_2$ that was size-selected as a cation and deposited and neutralized in a rare gas matrix.[32] Lisy and co-workers have obtained gas-phase IR photodissociation spectra for alkali cation−(water)$_x$(benzene)$_y$ complexes in the O−H stretch region.[33]

We recently have reported new measurements of the IR spectroscopy of transition metal−ion benzene complexes in the fingerprint region (600−1700 cm^{-1}) using a tunable free electron laser.[13−15] These studies demonstrated systematic shifts in the ring-based vibrations of these complexes.[15] A comprehensive study employing density functional theory (DFT) to investigate the structures, energetics, and vibrational frequencies of these complexes was also presented.[15] DFT found that some mono-ligand systems (Ti^+, Cr^+, Mn^+, and Cu^+) formed

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* Corresponding author. E-mail: maduncan@uga.edu.

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π-complexes with planar benzene in C_{6v} structures, while the bonding in other complexes was strong enough to distort the benzene planarity. Likewise, di-benzene complexes of some metals (Cr^+, Mn^+, and Co^+) formed D_{6h} complexes with planar benzene, while varying amounts of ring distortion occurred in other systems. Unfortunately, the resolution of the spectra was somewhat low, and these studies were limited to complexes with only one or two benzene molecules. In subsequent work, we have employed IR photodissociation spectroscopy for V^+(benzene)$_n$ complexes in the C−H stretch region using a higher resolution IR optical parametric oscillator/amplifier (OPO/OPA) laser system.[16] This latter study demonstrated that coordination is complete at two benzene molecules, and it showed that the onset of solvation with the third benzene molecule can be recognized by the appearance of the Fermi triad multiplet structure associated with free benzene.[16] The comparison with theory in both of these previous studies highlighted the difficulties in accurately describing the ground electronic state for such species.[15,16] In the present work, we extend these methods to study a late transition metal system, Ni^+(benzene)$_n$, where distorted structures are predicted and coordination and bonding interactions may be very different from those studied before.

Experimental Section

The experimental apparatus has been described previously.[34] Clusters are produced by laser vaporization in a pulsed nozzle source and mass analyzed in a reflectron time-of-flight spectrometer. A "cutaway" type rod holder[19,34] is used to limit metal atom recombination and enhance the formation of atomic cation−molecular complexes. The molecular beam is skimmed from the source chamber into a differentially pumped mass spectrometer. Cations that form directly in the source are pulse accelerated into the first flight tube where they are mass selected by pulsed deflection plates. The selected ions are intersected by the infrared output of a Nd:YAG (Continuum 8010) pumped IR-OPO/OPA system (LaserVision) in the turning region of the reflectron field. Photodissociation is enhanced on resonance with molecular vibrations of the ligand, and infrared photodissociation spectra are obtained by monitoring the resulting fragment yield versus the laser wavelength. Parent and fragment ions are mass analyzed in the second flight tube and detected using an electron multiplier tube and a digital oscilloscope (LeCroy Waverunner LT-342). Data are transferred to a PC via an IEEE-488 interface.

Results and Discussion

The mass spectrum of the cluster ions produced is shown in Figure 1. As expected from the cluster source configuration, the distribution is dominated by $Ni^+(C_6H_6)_n$ (n = 1,2,3,...) adducts. Clusters with multiple metal atoms, associated with multiple-decker sandwich or rice-ball type structures as seen by Kaya and co-workers,[22] are not produced efficiently in this configuration. Although clustering is efficient out to $n = 12$, a significant drop in intensity occurs after $n = 2$, indicating that the $n = 1,2$ complexes might be more stable than larger ones. Smaller intensity mass peaks are attributed to $Ni^+(H_2O)(C_6H_6)_n$, $Ni^+(C_6H_6)_nAr$, and $Ni_2^+(C_6H_6)_n$ ions.

The clusters are mass-selected and excited with the infrared laser in the C−H stretching region of benzene near 3100 cm^{-1}.[35] Unfortunately, this excitation produces virtually no photodissociation signals for the $Ni^+(C_6H_6)_{1,2}$ complexes. However, the inefficient photofragmentation for these complexes is not surprising because of their high binding energies (2.52 and 1.52 eV, or about 20 300 and 12 200 cm^{-1}, respectively),[20b] which are greater than the IR photon energy in this region. To improve photodissociation for these complexes, we employ the method of "rare gas tagging".[36−40] As shown in the past, attachment of argon to these metal−benzene ions increases their photodissociation yields because argon can be eliminated rather than the more strongly bound benzene ligands. Attachment of argon usually causes only minor perturbations on the vibrational modes of ions or ion−molecule complexes.[34,36−40] The binding energy of Ni^+−Ar is 0.55 eV (∼4436 cm^{-1}),[41] and therefore the argon binding should be less than this in these complexes. When the tagged ions are mass-selected and excited in the IR, essentially no photodissociation is observed again for $Ni^+(C_6H_6)Ar$, indicating that the Ar is still bound more strongly than the excitation energy. When a second Ar atom is added, however, efficient photofragmentation occurs via the loss of a single Ar. For $Ni^+(C_6H_6)_2Ar$, efficient photofragmentation is observed by the loss of Ar. Apparently, argon binds more weakly to this di-benzene complex. Vibrational resonances for both the mono- and the di-benzene complexes occur near 3100 cm^{-1}, as shown in Figure 2.

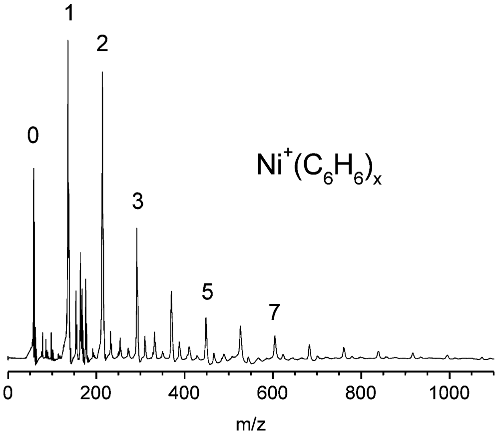

Figure 1. The mass spectrum of $Ni^+(C_6H_6)_x$ clusters, which is dominated by metal ion−benzene adducts. Lower intensity peaks between these adducts are attributed to $Ni^+(H_2O)(C_6H_6)_x$, $Ni^+(C_6H_6)_x$-Ar, and $Ni_2^+(C_6H_6)_x$ complexes.

As shown in Figure 3, the $n = 3$ complex and all larger ones studied dissociate efficiently without argon tagging via the elimination of benzene. This suggests that the binding energy of benzene in these complexes is less than the photon energy of about 3100 cm^{-1}. Such a decrease in the bond energy suggests that the third and subsequent benzene molecules are not bound directly to the metal cation. If this is true, the binding of these external benzene molecules should be roughly like that in pure benzene complexes that are bound by only van der Waals interactions. The dissociation energy of the benzene dimer is about 1000 cm^{-1}.[42−44] Therefore, the efficient photodissociation seen here for the $n = 3$ and larger complexes is consistent with such weak van der Waals bonding for the outer benzene molecules.

The IR spectrum of $Ni^+(C_6H_6)Ar_2$ contains a sharp doublet at 3093 and 3099 cm^{-1}, and each peak has a line width (fwhm) of about 6 cm^{-1}. The spectrum for the di-benzene complex $Ni^+(C_6H_6)_2Ar$ is somewhat similar to that of the mono-benzene species. It has one sharp feature at 3099 cm^{-1}, which is the same frequency as the right member of the doublet observed for $Ni^+(C_6H_6)Ar_2$. However, the overall band appears asymmetrical, with a shoulder on the lower frequency side near 3096 cm^{-1}. Due to its position and shape, this band could contain a doublet similar to that seen for $Ni^+(C_6H_6)Ar_2$ that is incompletely resolved. As noted above, complexes with $n = 3$ and

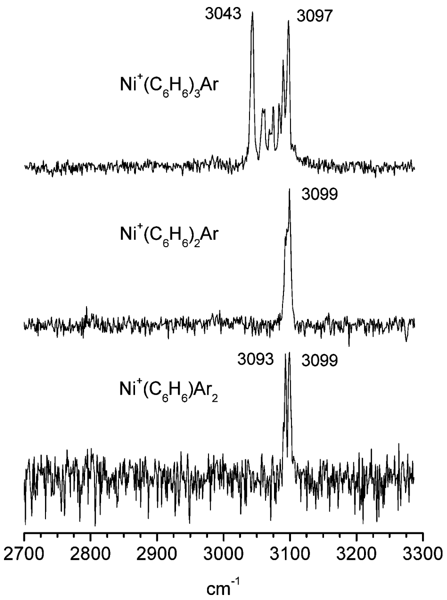

Figure 2. Infrared photodissociation spectra for $Ni^+(C_6H_6)Ar_2$, $Ni^+(C_6H_6)_2Ar$, and $Ni^+(C_6H_6)_3Ar$. The loss of Ar channel was monitored for these complexes. The multiplet in the spectra of $Ni^+(benzene)_3Ar$ is assigned to the benzene Fermi triad.

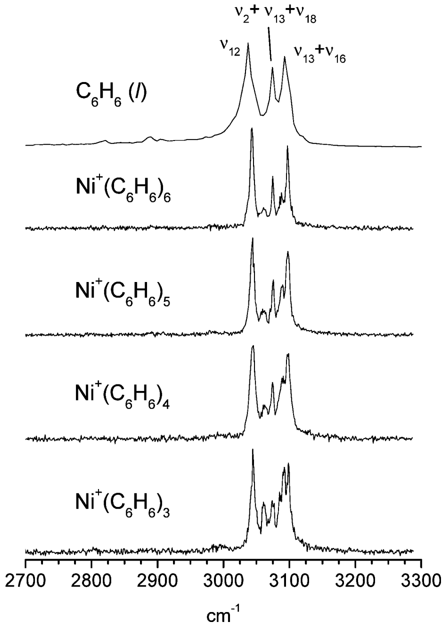

Figure 3. Infrared photodissociation spectra for $Ni^+(C_6H_6)_3$ through $Ni^+(C_6H_6)_6$ measured in the benzene-loss mass channel. The infrared absorption spectrum of benzene in the condensed phase is shown for comparison. The Fermi triad in liquid benzene has been labeled accordingly.

greater fragment efficiently without argon tagging. However, $Ni^+(C_6H_6)_3Ar$ has a spectrum that is similar to, but much sharper than, the one for $Ni^+(C_6H_6)_3$, and this tagged spectrum is therefore shown in Figure 2. This spectrum is quite different from those of $Ni^+(C_6H_6)Ar_2$ and $Ni^+(C_6H_6)_2Ar$. The resonances occur in the same wavelength region, but there is a multiplet of at least six peaks. Figure 3 shows the spectra for the $n = 3$ species measured without tagging in the benzene-loss channel as compared to those of several larger complexes. The complex multiplet pattern continues virtually unchanged for all of these larger clusters. The change in spectral pattern at $n = 3$ occurs at the same size as the decrease in the ligand binding energy noted above from the dissociation yield. This and the continuation of this pattern in the larger clusters suggest that this multiplet pattern in the IR results from external ligands not bound to the metal.

These spectral patterns can be analyzed in more detail by comparing them to the IR spectrum of benzene itself and to the corresponding spectra that we measured recently for $V^+(C_6H_6)_n$ complexes.[16] Benzene has a well-known multiplet structure in its C−H stretching region that comes from a Fermi resonance of the C−H stretch fundamental with overtone and combinations of lower frequency vibrations. A so-called Fermi triad of e_{1u} frequencies is found in both the IR spectrum of liquid benzene and that for the isolated benzene molecule in the gas phase. The triad consists of the ν_{12} C−H stretch fundamental and the $\nu_2 + \nu_{13} + \nu_{18}$ and $\nu_{13} + \nu_{16}$ combination bands, and it has bands at 3037, 3074, and 3093 cm^{-1}, respectively, for liquid benzene[35] and 3048, 3079, and 3101 cm^{-1} for benzene in the gas phase.[45] In the $Ni^+(C_6H_6)Ar_2$ and $Ni^+(C_6H_6)_2Ar$ spectra, the doublet bands seen are much closer together than those in the Fermi triad bands in benzene, suggesting that they should be assigned to different kinds of vibrational bands. We saw the same effect previously for $V^+(C_6H_6)_{1,2}$ species, whose spectra each had a single band.[16] Apparently, in these $n = 1$ and 2 complexes, the benzene ligands are bound strongly to the metal, and this interaction shifts the benzene-based vibrations away from their free-molecule frequencies. Shifts in these vibrations have been calculated by theory, and the overtone and combination bands move toward frequencies lower than the v_{12} C−H stretch fundamental.[15] These variable shifts for different vibrations remove the degeneracies found for the free molecule, and the $n = 1$ and 2 metal complexes do not have a Fermi triad band structure.

The $n = 3$ spectrum has prominent peaks on the low-frequency and high-frequency sides of the multiplet, at 3043 and 3097 cm^{-1}, respectively. Several less intense peaks appear between these, with the most intense lying at 3090 cm^{-1}. The outer multiplet members at 3043 and 3097 cm^{-1} lie very close to the outer members of the Fermi triad peaks in liquid (3037, 3093 cm^{-1}) and isolated gas-phase (3048, 3101 cm^{-1}) benzene. This same kind of structure persists in all of the larger clusters. As shown in Figure 3, the peak positions and intensity ratios seen here match well with those seen for the triad in liquid benzene. It therefore seems that the main aspects of the $n = 3$ multiplet spectrum arise from the onset of the Fermi triad structure at this cluster size. This is consistent with the decrease in binding energy noted above for this cluster size. Both of these factors indicate that the coordination of benzene in these clusters is two and that larger clusters have outer benzene molecules that are more weakly bound, acting essentially as solvent species. This is essentially the same behavior that we found previously for $V^+(C_6H_6)_n$ complexes.[16] Likewise, our recent UV photodissociation study of $Ni^+(C_6H_6)_n$ ($n = 1−8$) and other similar systems found evidence for a coordination number of two, as expected for sandwich complexes.[46] The structure of peaks near the center of these multiplets is more complex than it is in the Fermi triad and more complex than the structure that we found for $V^+(C_6H_6)_n$ complexes. We investigate the details of these features further below.

Having established the qualitative explanation for these spectra, it is informative to look more closely at the effects of metal bonding in the smaller ($n = 1$,2) complexes. To do this, we can use the results of the extensive DFT calculations that we published previously on this and other transition metal complexes with benzene.[15] From these previous results, we can assign the doublet peaks observed for the $n = 1$ complex to the

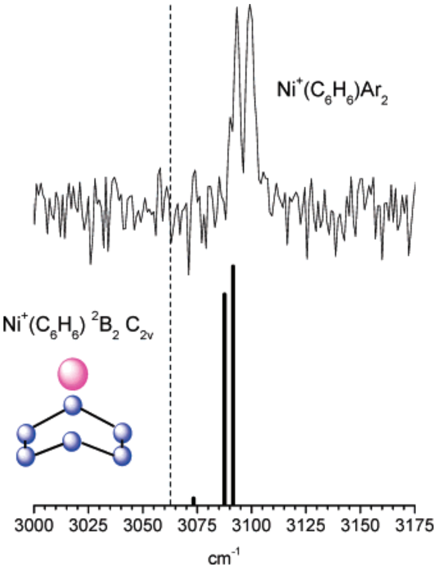

Figure 4. A comparison of the spectrum calculated for Ni$^+$(C$_6$H$_6$) with the experimental spectrum measured for Ni$^+$(C$_6$H$_6$)Ar$_2$. The dashed line indicates the rated frequency value of the ν_{12} C−H stretch fundamental of benzene in the absence of the Fermi triad.

ν_{12} C−H stretch of the benzene ligand in this complex, which is the only band expected to have significant IR intensity in this region. As shown in Figure 4, DFT predicts that two bands should be observed here because the benzene molecule is distorted from its planar geometry in this complex.[15] As shown in the figure, two carbons on opposite sides of the benzene ring are drawn upward toward the metal ion, and the hydrogens on these atoms are also shifted out of the plane, producing a complex with overall C_{2v} symmetry. The benzene ligand in the distorted structure has two types of nonequivalent hydrogens, and therefore there are two main IR-active C−H stretches predicted with frequencies at 3089 and 3093 cm^{-1}. As shown in the figure, the vibrational structure predicted for the ^{2}B$_2$ ground electronic state of this complex is in excellent agreement with the doublet observed. This provides convincing evidence that the Ni$^+$(C$_6$H$_6$) complex does indeed have the C_{2v} structure predicted by theory. A smaller intensity band predicted at 3073 cm^{-1} is apparently not detected with our limited sensitivity. It should be noted that the theory done for this complex did not include the argon atom, while tagging was necessary to see the spectrum. Apparently, the argon does not induce a major shift in the structure of this complex or its spectrum.

Figure 5 shows the comparison between experiment and theory for the Ni$^+$(C$_6$H$_6$)$_2$ complex. In this complex, DFT predicts two geometries (shown in the figure) that have close energetics, both with doublet spin states. The lower energy state (^{2}A) has C_1 symmetry in which the Ni cation sits over the η^3 position of both benzene rings, but the rings are trans-parallel to each other. This state is predicted to be bound (with respect to elimination of the last ligand) by 33.7 kcal/mol. The second state (^{2}B$_{2g}$) has D_{2h} symmetry, in which the Ni ion resides in the η^6 position of both rings. The benzenes are distorted like that in the $n = 1$ complex, with two carbons opposite each other on each ring pulled toward the ion. The rings are in an eclipsed configuration with each carbon on one ring aligned with a carbon on the opposite ring. According to DFT, this latter structure lies 5.4 kcal higher in energy than the C_1 structure, with a binding energy of $D_0 = 28.3$ kcal/mol. Figure 5 shows the vibrational bands predicted for the ^{2}A species in red and those for the ^{2}B$_{2g}$ species in blue. As indicated, the structure predicted for the ^{2}B$_{2g}$ state appears to agree much better with the experiment. Two bands are predicted with a close spacing, corresponding to the suspected unresolved doublet in the experimental spectrum. Two lower intensity bands predicted for the ^{2}B$_{2g}$ state are not observed, but these could be missed with our limited sensitivity. The spectrum predicted for the ^{2}A state does not match the experiment, even though theory predicts this state to lie at lower energy. Not only are the frequencies predicted too far to the red, but the multiplet of four peaks with roughly equal intensities is clearly not observed. The experiment therefore favors the D_{2h} structure with two benzene rings distorted in the same way as the single ring in the $n = 1$ complex.

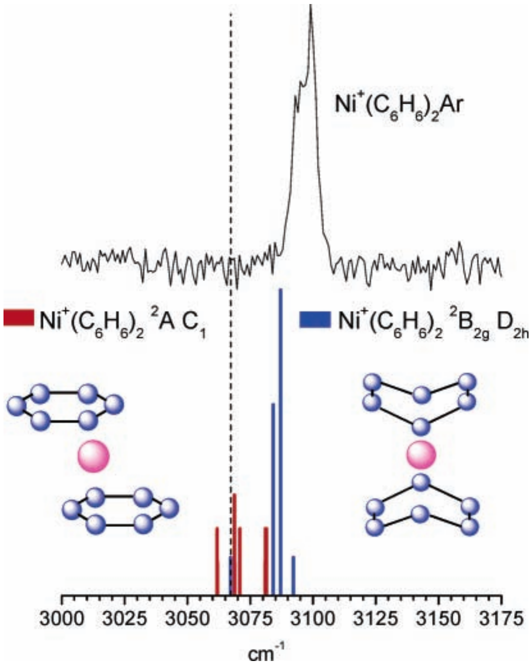

Figure 5. A comparison of the spectrum calculated for the two possible structures of Ni$^+$(C$_6$H$_6$)$_2$ with the experimental spectrum measured for Ni$^+$(C$_6$H$_6$)$_2$Ar. The predicted bands are shown with their relative intensities. The dashed line indicates the rated frequency value of the ν_{12} C−H stretch fundamental of benzene in the absence of the Fermi triad.

It is interesting that the lowest structure and electronic state predicted by theory is apparently not observed experimentally. In our previous study of Ni$^+$(C$_6$H$_6$)$_2$ in the fingerprint region of the IR,[15] we measured a band corresponding to the υ_{19} ring-distortion mode near 1495 cm^{-1}. The frequency shift of this band gave no indication at all that the complex might have any structure other than the predicted C_1 geometry. However, the IR spectra predicted for the υ_{19} band region are almost identical for the C_1 and D_{2h} structures. Within the broad line width of the free electron laser, we could not have seen any difference between these species in those experiments. The C−H stretch region for this complex turns out to provide a clearer signature for the structure of the complex, and then we are able to recognize the disparity between experiment and theory. This is the first example in our studies of metal−benzene complexes where we have found such a clear difference between the structure predicted and that observed. However, we found somewhat related disagreements between experiment and DFT predictions in our work on V$^+$(C$_6$H$_6$)$_{1,2}$ complexes.[16] In these systems, the predicted ground state for both the $n = 1$ and 2 species is a triplet, correlating to the ^{3}F state of isolated V$^+$. However, in both cases, the experimental results matched the spectra predicted for species with a quintet spin state, correlating to the ^{5}D state of V$^+$. DFT calculations apparently misjudged the relative energetics of these two spin configurations for the vanadium complexes. This result is not too surprising, as it is well known that DFT has problems with open-shell systems and the relative energetics of high-spin versus low-spin configurations.[47] In the present case of $Ni^+(C_6H_6)_2$, however, there is apparently also a problem with the relative energetics of two geometries that both have the same spin configuration.

It is interesting to compare the vibrational bands observed for these complexes to those of the free benzene molecule to investigate the effect of metal binding in this organometallic system. Because of the presence of a Fermi triad in free benzene, this comparison is not straightforward. However, the frequency value for the ν_{12} mode in benzene calculated in the absence of the Fermi triad (3063 cm^{-1})[35] can be used to investigate the subsequent shift caused by binding to the metal cation. The position of this υ_{12} band is shown in both Figures 4 and 5 as a dashed line for comparison to our spectra for the $n = 1$ and 2 complexes. It can be seen that the bands measured for both complexes are shifted about 30 cm^{-1} to higher frequency than the C−H stretch in isolated benzene. Previous work on $V^+(C_6H_6)_{1,2}$ demonstrated similar blue shifts of about 25 cm^{-1},[16] and we have also seen a similar blue shift in the $Si^+(C_6H_6)_{1,2}$ spectra.[48] Although the Ni^+, V^+, and Si^+ systems were all measured using Ar tagging, a shift due to the Ar atom would be small (~5 cm^{-1}) and generally would go toward lower frequency.[34]

A blue-shift in these C−H frequencies is at first glance a little surprising. In the classic Dewar−Chatt−Duncanson model of π-bonding,[49−51] the interaction is composed of σ-donation of ligand electron density into the empty metal d orbitals and π back-bonding of d electron density into the π^* antibonding orbitals of the ligand. Both of these effects weaken the bonding on the benzene molecule and are expected to shift vibrational frequencies to lower values. In our recent studies of $M^+(C_6H_6)_x$ complexes in the fingerprint region, the ring distortion modes as well as the in-plane C−H bends shifted to lower frequencies, consistent with this reasoning.[13,15] Likewise, in our previous work on metal cation−acetylene complexes of Co^+ and Ni^+, the asymmetric and symmetric C−H stretches were observed to red-shift.[52] This tendency appears to be reversed for the C−H stretches of V^+ and Ni^+ complexes with benzene. However, as we noted previously,[16] a similar blue shift has been observed for the C−H stretches of the benzene cation by Dopfer and co-workers in their IR studies of nonmetal $C_6H_6{}^+{-}L$ (L = Ar, N_2, CH_4) complexes.[53] The IR spectra of these complexes yielded a ν_{12} fundamental of 3095 cm^{-1}, approximately 30 cm^{-1} higher than that of neutral benzene. Apparently, the C−H bonds become stiffer upon removal of an electron from the HOMO e_{1g} orbital of benzene. The blue-shift observed in $Ni^+(C_6H_6)_n$ complexes is therefore likely due to a polarization of electron density from the benzene toward the metal ion in these complexes. The ionization potential of nickel (7.64 eV)[54] is much less than that of benzene (9.24 eV),[55] and therefore it is not surprising that such an effect would occur in these systems.

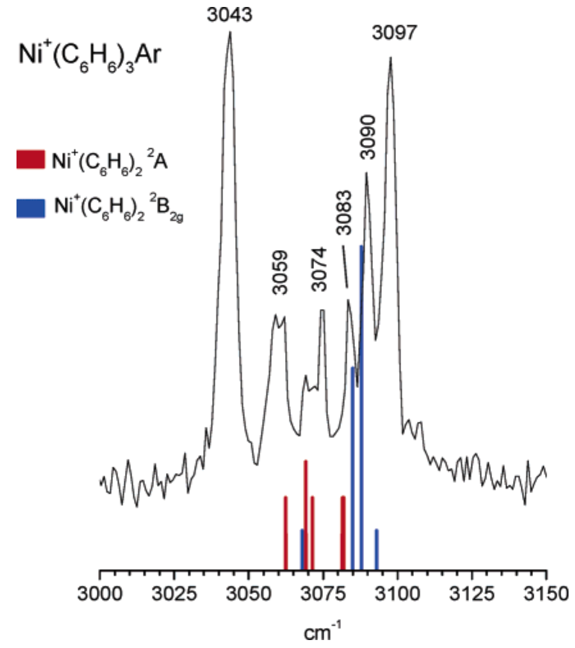

Figure 6. The calculated spectrum for $Ni^+(C_6H_6)_2$ as compared to the experimental spectrum of $Ni^+(C_6H_6)_3Ar$. The peaks associated with the Fermi triad have been labeled accordingly.

Having discussed the structures and spectra of $Ni^+(C_6H_6)_2$, it is now possible to consider $Ni^+(C_6H_6)_3Ar$ in more detail. A magnification of this spectrum is shown in Figure 6. As noted above, the two outer peaks in this multiplet can be associated with the corresponding peaks for the Fermi triad, but there are more bands between these two than we would expect. If the spectrum of this $n = 3$ species represents an $n = 2$ sandwich with one external molecule, then we would expect the IR spectrum to contain a superposition of these two components. The Fermi triad peaks would come from the external molecule, and the so-called "core" $n = 2$ ion would be expected to contribute peaks like those in the spectrum of the $n = 2$ complex. The outermost peaks at 3043 and 3097 cm^{-1} can be associated with the outer members of the Fermi triad based on their positions. Corresponding to these, we can identify by position and relative intensity an inner band at 3074 that can be assigned as the third member of the triad. The other bands presumably correspond to the $n = 2$ core ion, and therefore we have also plotted the predicted bands for the two geometries of this ion in the figure. The bands at 3083 and 3090 cm^{-1} are slightly red-shifted from those in the $n = 2$ spectrum, with a spacing about the same as that expected for the $^2B_{2g}$ state of the D_{2h} complex. A small red shift is reasonable because of solvation, and therefore we assign these bands to the $^2B_{2g}$ core ion. This accounts for all of the main bands in this spectrum except one at 3059 cm^{-1}. An assignment for this last band is not at all obvious. As shown in the figure, additional minor bands of the $^2B_{2g}$ state are also expected in this general region, but these were not detected in the $n = 2$ spectrum. It is perhaps possible that the intensity of one such band increases in the $n = 3$ complex, making it possible to detect this. Another possibility is that there are isomeric species present in the ^2A state for the C_1 complex. As shown in the figure, bands from this state are also possible in this general wavelength range. Unfortunately, we have no theory for the $n = 3$ complex that could clarify this situation. Based on our previous experience with theory on similar systems, it may be very difficult to obtain such information. Figure 3 shows that the bands that we assigned here for the $n = 3$ complex, as well as the unassigned 3059 cm^{-1} band, are present in the spectra of all of the larger ($n = 4-6$) complexes that we have studied. Whatever the core ion character is in the $n = 3$ species, this same character is apparently present in all of the larger clusters.

Conclusion

We report here the first gas-phase infrared spectra for $Ni^+(C_6H_6)Ar_2$, $Ni^+(C_6H_6)_{2,3}Ar$, and $Ni^+(C_6H_6)_{3-6}$ complexes in the C−H stretch region. Infrared photodissociation is inefficient for the $n = 1$ and 2 complexes, consistent with their strong ligand

TABLE 1: Experimental and Theoretical Vibrational Spectra for $Ni^+(C_6H_6)_n$ Complexes[a]

complex	elect. state	theory	experiment
C_6H_6 (l)	$^1A_{1g}$ (D_{6h})	3063[b]	3037, 3074, 3093[c]
C_6H_6 (g)	$^1A_{1g}$ (D_{6h})	3063[b]	3048, 3079, 3101[d]
$Ni^+(C_6H_6)$	$^2B_2$ (C_{2v})	3073, 3089, 3093	3093, 3099[e]
$Ni^+(C_6H_6)_2$	2A (C_1)	3062, 3069, 3071, 3081, 3082	3096[e]
$Ni^+(C_6H_6)_2$	$^2B_{2g}$ (D_{2h})	3067, 3084, 3087, 3092	3096[e]
$Ni^+(C_6H_6)_3$			3043, 3059, 3074,[e] 3083, 3090, 3097
			3045, 3062, 3074, 3085, 3091, 3099
$Ni^+(C_6H_6)_4$			3044, 3062, 3074, 3089, 3098
$Ni^+(C_6H_6)_5$			3044, 3060, 3076, 3089, 3098
$Ni^+(C_6H_6)_6$			3044, 3061, 3075, 3088, 3097

[a] All band positions are in cm^{-1}. The n=3 data is given twice for spectra measured with and without argon tagging. [b] Selected frequency value rating in the absence of Fermi triad (NIST).[35] [c] Reference 35. [d] Reference 45. [e] Band positions measured for argon-tagged species.

binding. The rare gas tagging experiments make it possible to detect IR spectra for these species. The $Ni^+(C_6H_6)Ar_2$ complex yields a simple spectrum with a doublet shifted to higher frequency from that of neutral benzene. The $Ni^+(C_6H_6)_2Ar$ has a spectrum with a broad band apparently indicating an unresolved doublet, and this is also shifted to higher frequency than neutral benzene. Once the number of benzene ligands exceeds the coordination number of two, the complexes dissociate in the IR via the loss of benzene, and a new a multiplet structure attributed to the Fermi triad of benzene is observed. This confirms that a stable core is established at $n = 2$, consistent with the expected di-benzene sandwich complex. Subsequent molecules act as solvent for the sandwich core.

The C−H stretching band measured for $Ni^+(C_6H_6)Ar_2$ matches the predicted doublet structure for the $^2B_2$ C_{2v} structure, which is the ground state predicted by DFT for the $Ni^+(C_6H_6)$ complex. Theory has previously predicted a distortion of the benzene in mono-ligand complexes with V^+, Fe^+, Co^+, and Ni^+,[15] but this is the first definitive evidence that such distortion occurs. The vanadium complex that we have studied previously had a single IR-active band, but the greater distortion in the Ni^+ complex leads to additional active C−H stretches. The $Ni^+(C_6H_6)_2Ar$ spectrum matches that calculated for the $^2B_{2g}$ D_{2h} structure of $Ni^+(C_6H_6)_2$, which is not its predicted ground state. In this complex, both benzene rings are distorted in the same way seen for the mono-benzene complex.

We have now studied an early transition metal system (vanadium−benzene) and the present late transition metal system with IR spectroscopy in the C−H stretching region. In both cases, the metal ion coordination is two and the Fermi triad structure appears for the $n = 3$ and larger complexes. Blue-shifted bands are observed for the C−H stretches in all of the $n = 1$ and 2 complexes, consistent with polarization of electron density from the benzene toward the metal ion. In both systems, DFT theory leads to correct predictions for the structures and ground states of some ions and to erroneous predictions for others. The relative stability of different spin states and different geometries in these systems continues to be a challenging issue for theory.

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