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LETTERS

Structure, Coordination, and Solvation of V^+(benzene)$_n$ Complexes via Gas Phase Infrared Spectroscopy

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$V^+(C_6H_6)_n$ ($n = 1-4$) and $V^+(C_6H_6)_nAr$ ($n = 1, 2$) complexes are produced by laser vaporization in a pulsed nozzle cluster source. The clusters are mass-selected and studied by infrared laser photodissociation spectroscopy in the C−H stretch region of benzene. Photodissociation of $V^+(C_6H_6)_n$ complexes occurs by the elimination of intact neutral benzene molecules, whereas $V^+(C_6H_6)_nAr$ complexes lose Ar. The dissociation process is enhanced on vibrational resonances and the spectrum is obtained by monitoring 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 occurs at $n = 3$, confirming that two ligands complete the coordination sphere and that additional benzenes act as solvent. The comparison between experiment and theory provides fascinating new insight into the bonding in these prototypical organometallic complexes.

Introduction

Transition metal ion−molecule complexes that are produced and studied in the gas phase are convenient examples of metal−ligand interactions and metal ion solvation.[1−4] Aromatic π-bonded complexes are relevant in many catalytic and biological processes.[5−8] These complexes are also interesting because they form sandwich structures.[7,8] Dibenzene chromium was among the first species to be synthesized using conventional techniques.[9] Gas phase complexes can in principle be compared to those produced by conventional synthesis. Unfortunately, however, there are few spectroscopic studies that provide insight into the structures and bonding of these species. Conventional infrared (IR) spectroscopy has been applied to condensed phase complexes,[10−12] but such measurements are difficult in the gas phase. However, gas phase measurements avoid complications from solvents or solid environments, and provide an ideal comparison to theory. We have recently measured IR spectroscopy for several metal ion−benzene complexes in the far-IR fingerprint region using a tunable free-electron laser.[13−15] In the present work, we extend these vibrational spectroscopy studies for the first time to the C−H stretch region. The vanadium−benzene system illustrates the effects of metal binding, sandwich formation and solvation on these vibrational modes.

Metal−benzene sandwiches, including dibenzene vanadium, are familiar in the condensed phase and in gas phase ion chemistry. In the latter area, collisional studies[16] and equilibrium mass spectrometry[17] have investigated bonding energetics, and theory has studied the details of electronic and geometric structure.[17−24] As shown by Kaya and co-workers, gas phase V_n(benzene)$_m$ complexes form multiple-decker sandwiches.[25] Bowers and co-workers probed these complexes with ion mobility measurements.[26] Kaya and co-workers reported a partial IR spectrum for the 1:2 complex that was size-selected as a cation, and then trapped in a rare gas matrix and neutralized.[27] However, there are few studies of gas phase spectroscopy for

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metal−benzene complexes. Electronic photodissociation spectroscopy has produced broad resonances associated with metal−ligand charge transfer,[28] and photoelectron spectroscopy of anions provides electron affinities.[25b,29] Lisy and co-workers have measured IR spectra of mixed-ligand alkali cation−(water)$_n$(benzene)$_m$ complexes in the O−H stretch region,[30] and we have recently reported the vibrational spectra of several transition metal ion−benzene complexes in the 600−1700 cm^{-1} region.[13−15] These latter studies included a detailed investigation of the spectrum of $V^+(C_6H_6)_{1,2}$ and theoretical calculations of the structures and vibrational frequencies of these complexes.[13,15] Unfortunately, these measurements were limited to the lower frequency region of the spectrum, and only complexes with one or two ligands could be studied. Further insight is expected here as these studies are extended into the C−H stretching region of the spectrum and to complexes with multiple benzene ligands.

Experimental Section

The experimental apparatus has been described previously.[31] Clusters are produced by laser vaporization at 355 nm in a pulsed nozzle cluster source and mass analyzed in a reflectron time-of-flight mass spectrometer. By using a "cutaway" type rod holder a free expansion with excess benzene produces clusters primarily of $V^+(C_6H_6)_n$ and $V^+(C_6H_6)_nAr$ (n = 1, 2, 3, ...). Metal atom recombination is not efficient in this source configuration and multiple-decker sandwich clusters are not produced efficiently. The molecular beam is skimmed from the source chamber into a differentially pumped mass spectrometer chamber. Ions are pulse accelerated into the first flight tube, and mass selected by pulsed deflection plates located just before the reflection region. The selected ions are intersected by the infrared output of a Nd:YAG pumped optical parametric oscillator/amplifier (OPO/OPA, 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

IR excitation produces essentially no photodissociation signals for the $V^+(C_6H_6)_{1,2}$ complexes in the region of the IR-active C−H stretches of benzene near 3100 cm^{-1}.[32] The inefficiency of photodissociation for these complexes is consistent with their known binding energies (2.42 and 2.55 eV, respectively),[16b] which are greater than the one-photon excitation energy here. To probe these complexes more effectively, we use the method of rare gas tagging with argon.[31,33−37] The binding energy of V^+−Ar is 0.38 eV (∼3060 cm^{-1}),[38] and the binding energy of argon in these complexes should be less than this value. Therefore, single photon photodissociation should be possible by elimination of argon when excitation occurs near 3100 cm^{-1}. As shown in the past, tagging increases the photodissociation efficiency and argon is usually a minor perturbation on the spectrum of the complex. We find efficient photodissociation of $V^+(C_6H_6)Ar$ and $V^+(C_6H_6)_2Ar$, which occurs by the loss of argon. Vibrational resonances occur for these species near 3100 cm^{-1}, as shown in Figure 1. Beginning at the n = 3 complex and continuing for all larger complexes studied, the dissociation yield is substantial without argon tagging. The sudden increase in dissociation efficiency at n = 3 and beyond is consistent with the presence of benzene molecules not attached to the metal ion. The binding energy of such external ligands should approximate that of the benzene dimer (about 800 cm^{-1}),[39] and so these external molecules can be eliminated via a one-photon process. Sharp vibrational spectra are measured for these complexes also in the 3100 cm^{-1} region. Spectra for the n = 3−4 complexes are shown in Figures 1 and 2, and the line positions are given in Table 1.

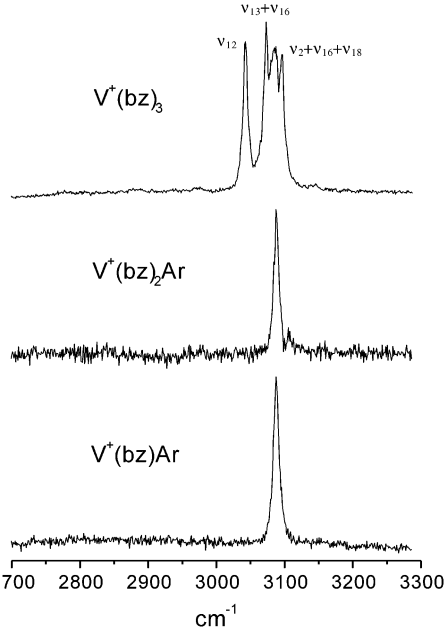

Figure 1. Infrared photodissociation spectra for V^+(benzene)Ar, V^+(benzene)$_2$Ar, and V^+(benzene)$_3$. The multiplet in the spectrum of V^+(benzene)$_3$ is assigned to the benzene Fermi triad.

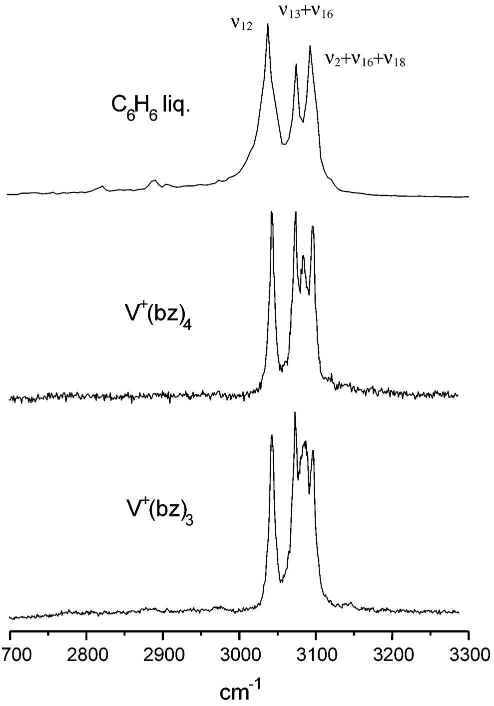

Figure 2. Infrared photodissociation spectra for V^+(benzene)$_3$ and V^+(benzene)$_4$ measured in the C_6H_6 elimination channel. The infrared absorption spectrum of liquid benzene is shown for comparison.

The IR photodissociation spectrum of $V^+(C_6H_6)Ar$ monitored in the loss of Ar channel is shown in Figure 1. In the range from 2700 to 3300 cm^{-1} there is only one main peak. On the basis of the previous results of density functional theory,[13,15]

TABLE 1: Experimental and Theoretical Line Positions for Various Complexes

complex	elect. state	theoretical line position (cm^{-1})	experimental line position (cm^{-1})
C_6H_6 (*l*)	$^1A_{1g}$	3063[a]	3037, 3074, 3093[b]
C_6H_6 (*g*)	$^1A_{1g}$	3063[a]	3048, 3079, 3101[c]
$V^+(C_6H_6)$	$^5B_1$ (C_{2v})	3082, 3087	3088
$V^+(C_6H_6)$	$^3A_2$ (C_{2v})	3066, 3079, 3090, 3093	3088
$V^+(C_6H_6)_2$	$^3B_{3g}$ (D_{2h})	3087, 3097, 3099	3088, 3108
$V^+(C_6H_6)_2$	$^5B_{2g}$ (D_{2h})	3087, 3091	3088, 3108
$V^+(C_6H_6)_3$			3043, 3073, 3086, 3096
$V^+(C_6H_6)_4$			3043, 3074, 3085, 3096

[a] Selected frequency value rating in the absence of Fermi triad (NIST).[32] [b] Reference 32. [c] Reference 40.

this can be assigned to the ν_{12} C−H stretch of the benzene ligand in this complex, which is the only band expected to have strong IR intensity in this region. The peak occurs at 3088 cm^{-1} with a line width (FWHM) of ~12 cm^{-1}. A large peak with this same frequency and approximate line width is also recorded in the argon-loss channel for $V^+(C_6H_6)_2Ar$. For this complex a second smaller but reproducible peak is seen at 3108 cm^{-1}. For the $V^+(C_6H_6)_3$ complex, photodissociation occurs efficiently by the loss of benzene and no tagging experiments are required. The spectrum of this complex is dramatically different from those of the smaller complexes, containing a multiplet of at least four distinct features. In the center of this multiplet a band occurs at 3086 cm^{-1}, which is essentially the same position as the main band found for the $V^+(C_6H_6)Ar$ and $V^+(C_6H_6)_2Ar$ complexes. The multiplet and the band common to the $n = 1$, 2 complexes appear essentially unchanged in the spectra of the $n = 3$, 4 clusters.

Figure 2 compares the spectra of $V^+(C_6H_6)_3$ and $V^+(C_6H_6)_4$ to the literature spectrum for liquid benzene. The liquid benzene spectrum has essentially the same appearance as the gas phase spectrum, containing three peaks at 3037, 3074, and 3093 cm^{-1}.[32] This multiplet arises from the well-known Fermi triad of e_{1u} frequencies composed of the ν_{12} fundamental and the $\nu_{13} + \nu_{16}$ and $\nu_2 + \nu_{13} + \nu_{18}$ combination bands. These bands occur at 3048, 3079, and 3101 cm^{-1} in the gas phase.[40] It is apparent from the band positions and their intensities that the liquid benzene spectrum is essentially reproduced as the multiplet observed for the $n = 3$ and 4 complexes. In addition to the features at 3086 ($n = 3$) or 3085 ($n = 4$) cm^{-1} corresponding to the 3088 cm^{-1} band in the smaller clusters, the multiplets have bands at 3043, 3073, and 3096 cm^{-1} ($n = 3$) or 3043, 3074, and 3096 cm^{-1} ($n = 4$), all of which are within 4−6 cm^{-1} of corresponding bands in the liquid spectrum. The simplest interpretation of these spectra, therefore, is that the $n = 1$ and 2 complexes have benzene molecules attached directly to the metal cation, with concomitant shifts in their vibrational modes. These shifts, even though they may be small, are enough to remove the degeneracies that cause the Fermi triad, and this pattern simplifies to the single band from the ν_{12} fundamental expected here. At clusters beyond $n = 2$, the ν_{12} fundamental band associated with the "core" complex persists, and the additional pattern associated with the triad reappears. This indicates the presence of benzene molecules without any serious perturbation on their spectra, i.e., those not attached to the metal. The coordination to the vanadium cation must therefore be two benzene molecules, exactly as expected for the sandwich complex, and the benzenes beyond these two act as solvating molecules in the cluster.

In the $n = 1$, 2 complexes, it is interesting to compare the vibrational mode observed to that of the free benzene molecule to investigate the effect of metal binding. Because of the Fermi resonance in isolated benzene, this comparison is not straightforward. However, the rated frequency value for the ν_{12} mode in free benzene in the absence of the Fermi resonance is 3063 cm^{-1}.[32] This indicates that there is a 25 cm^{-1} shift to higher frequency for the ν_{12} mode in the $V^+(C_6H_6)_{1,2}$ complexes. Though the presence of argon may introduce a small shift in vibrational bands, such a shift would usually go to the red.[31] Because the core band position for $n = 1$, 2 is essentially unchanged in the $n = 3$, 4 complexes, which have no argon, it seems that argon plays a negligible role in this band position. However, the observation of a blue shift compared to the free molecule is somewhat surprising. In the classic Dewar−Chatt−Duncanson picture of π-bonding,[41−43] the metal−ligand interaction can be viewed from the standpoint of σ-donation of ligand bonding electron density into empty metal d orbitals and π back-bonding of d electron density into the π^* antibonding orbitals. Both of these effects weaken the bonding on the benzene moiety and thus are expected to shift vibrational frequencies to *lower* values. In our recent studies of $M^+(C_6H_6)_n$ complexes, the ring distortion modes and 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 Ni^+ and Co^+, the symmetric and asymmetric C−H stretches were also red shifted.[44] However, the tendency is apparently reversed here for the C−H stretches in the vanadium−benzene complexes. However, such a blue shift has been seen previously for the C−H stretches of benzene by Dopfer and co-workers in their recent IR spectroscopy work on $C_6H_6{}^+{-}L$ (L = Ar, N_2, CH_4) complexes.[45] IR photodissociation spectroscopy of such benzene *cation* complexes yielded ν_{12} resonances near 3095 cm^{-1}, some 30 cm^{-1} higher than the frequency of the neutral benzene species. This indicates that the C−H bonds become stiffer upon removal of an electron from the HOMO e_{1g} orbital of benzene. V^+ has a d^4 (^5D) configuration, with low d electron density compared to the later transition metals. This deficiency suggests that σ-donation will be more important than π back-bonding in its metal−benzene interaction, resulting in greater charge transfer from the benzene toward the metal cation. In this sense, the benzene will become partially charged, as in the cation, and a similar blue shift in the C−H stretches is reasonable.

In addition to the shifts induced by metal binding, the loss of the Fermi triad in the $n = 1$ and 2 complexes is also an interesting feature of these spectra. If we derive a coupling strength for the ν_{12} mode with the $\nu_{13} + \nu_{16}$ combination mode on the basis of the observed band splittings in the free benzene molecule[46] and note that a Fermi resonance splitting would have to be greater than our line width of about 5 cm^{-1} to be detected, we can evaluate the likely proximity of these same vibrations in the metal−benzene complexes. From this analysis, we can conclude that the ν_{12} and $\nu_{13} + \nu_{16}$ combination modes, which are exactly degenerate in benzene, must be more than 18 cm^{-1} apart in the metal−benzene complex. According to the DFT results for the monobenzene complex,[15] the $\nu_{13} + \nu_{16}$ combination occurs at 2966 cm^{-1} whereas the ν_{12} mode has a frequency in the 3080−3090 cm^{-1} region, depending on the spin state (see below). ν_{13} and ν_{16} are ring-distortion modes, and these shift substantially in the metal complexes because the metal binding distorts the benzene ring into a nonplanar structure (see Figure 3), whereas the C−H stretching modes correlating to the ν_{12} in benzene shift to higher frequency, as noted above. It is therefore reasonable that these vibrations move away from each other in the metal complexes, resulting in the loss of the Fermi resonance.

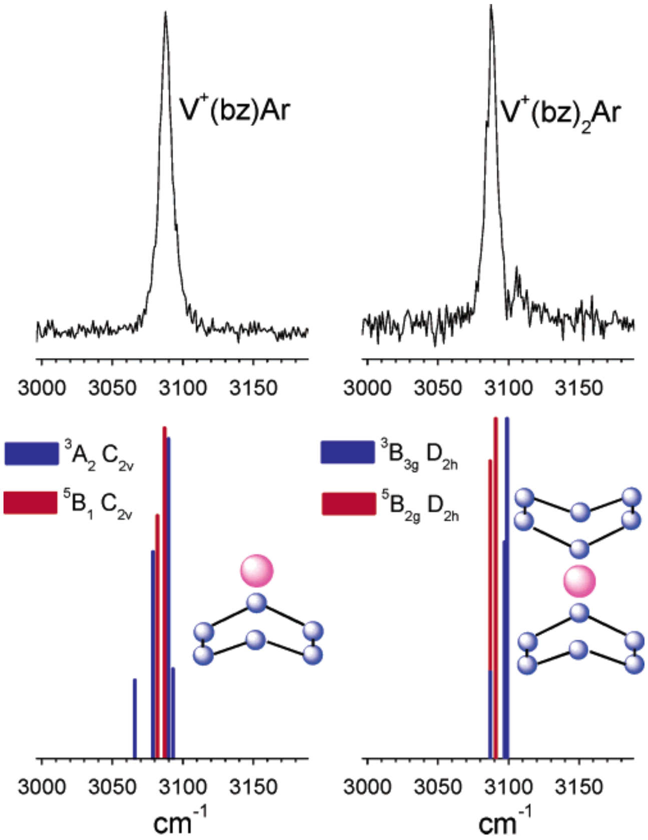

Figure 3. Calculated spectra for V$^+$(benzene) and V$^+$(benzene)$_2$ compared to the experimental spectra of V$^+$(benzene)Ar and V$^+$(benzene)$_2$Ar. Predicted intensities have been normalized for direct comparison. The molecular models have had their hydrogens removed and the distortion of the benzene ring has been exaggerated.

Our previous work in the far IR on metal ion−benzene complexes featured extensive comparison with theoretical calculations.[13,15] The molecular structures, harmonic vibrational frequencies, and infrared absorption intensities were calculated for a variety of M$^+$(benzene)$_{1,2}$ complexes of the first-row transition metals via density functional theory (DFT) employing the Becke-3 Lee−Yang−Parr (B3LYP) functional and the 6-311++G(d,p) basis set.[15] Although the trends in frequency shifts were predicted qualitatively, several discrepancies occurred between predicted IR spectra and those measured. Some issues could not be resolved due to experimental uncertainties. As the ions in that experiment were generated by photoionization (ArF, 193 nm) of neutral complexes, it was not clear that the spectra obtained were for complexes in their ground electronic state. The inherent line width of the free electron laser used in those multiphoton experiments, coupled with the possibility of thermally and/or electronically excited ions, led to spectral features with line widths ranging from 20 to 50 cm^{-1}. These limitations caused ambiguities in the ground state symmetry and electronic structure assignment for these complexes. In the present experiments, ions are produced without photoionization and are cooled by supersonic expansion after their formation. The OPO laser line width is substantially narrower (0.3 cm^{-1}), resulting in sharper lines than we obtained previously. It is therefore interesting to compare these data on the C−H stretch vibrations to our previous theoretical predictions.

In the previous calculations,[13,15] the vanadium ion−benzene monomer complex was allowed to deviate from C_{6v} to C_{2v} symmetry by distortion of the benzene ring to obtain all real frequencies. The metal cation was assumed to bind to the central region of the benzene aromatic ring for both mono- and dibenzene complexes. Frequencies were scaled on the basis of comparison of the calculated and experimental spectra of C$_6$H$_6$. The calculated spectra for V$^+$(C$_6$H$_6$) and V$^+$(C$_6$H$_6$)$_2$ are compared to the experimental IR photodissociation spectra of V$^+$(C$_6$H$_6$)Ar and V$^+$(C$_6$H$_6$)$_2$Ar in Figure 3.

Two electronic configurations, each with C_{2v} symmetry because benzene is slightly distorted by the metal binding, were calculated as candidates for the ground state of V$^+$(C$_6$H$_6$).[15] The ^{3}A$_2$ state (D_0 for loss of benzene = 48.4 kcal/mol) was predicted to lie slightly lower in energy than the ^{5}B$_1$ state (D_0 = 47.5 kcal/mol).[15] The binding of benzene is therefore predicted to change the spin configuration on V$^+$, which is a quintet in its isolated form. These two spin states have essentially the same geometric structure, but differences in the electronic structure lead to different vibrational band patterns for each. The predicted IR spectra for these two spin states are shown in Figure 3. The triplet is expected to have a quartet multiplet structure in the C−H stretching region, with outer peaks spaced by about 30 cm^{-1}. The quintet is predicted to have only two C−H stretching modes with similar band intensities more closely spaced at 3082 and 3087 cm^{-1}. In the experimental spectrum, only one peak is observed, with a line width of about 20 cm^{-1}, which is much broader than the laser line width. Even with this line width, we should have been able to see a widely spaced multiplet structure like that predicted for the triplet, but we do not. However, the two predicted peaks for the quintet species have such a small spacing (5 cm^{-1}) that these bands could easily be present but unresolved. Our spectrum therefore seems to be more consistent with the quintet electronic state, even though the triplet state is predicted to be more stable. This is not too surprising, because the energy difference predicted between the triplet and quintet species is quite small. Consistent with these observations, the vibrations in the lower frequency region observed for V$^+$(C$_6$H$_6$) in our previous work also agreed with those predicted for the quintet ground state for this species.[13,15]

Although the measured spectra for V$^+$(C$_6$H$_6$)Ar and V$^+$(C$_6$H$_6$)$_2$Ar are quite similar, the theoretical predictions for V$^+$(C$_6$H$_6$) and V$^+$(C$_6$H$_6$)$_2$ are quite different. A low-spin state like that predicted for the monobenzene complex is also predicted as the second benzene ligand is attached to the vanadium ion, yielding a (^{3}B$_{3g}$) D_{2h} ground state. However, the energetic stabilization of this state is much more significant, and it is calculated to lie nearly 30 kcal/mol lower in energy than the corresponding (^{5}B$_{2g}$) D_{2h} state.[13,15] However, this triplet species is predicted to have *three* IR-active bands in the C−H stretch region at 3087, 3097, and 3099 cm^{-1}.[15] Although the latter two bands are too close to resolve with our line width, the 10 cm^{-1} splitting between the 3087 and 3097 cm^{-1} features is again great enough that we should be able to detect this splitting, but we do not. A small shift from the predicted band positions may occur in these complexes because of the presence of the argon tag. However, if there is any perturbation from argon it should be greater for the monobenzene complex, where the binding can occur on the metal and is likely stronger. In the dibenzene complex, because the coordination is apparently filled, the argon must be bound externally to benzene through weaker van der Waals forces. Additionally, it is not clear that small shifts because of the argon would remove the multiplet predicted for the triplet state. We are therefore puzzled by the apparent poor agreement between the measured spectrum and the predicted one. A possible explanation is found in the prediction of theory for the quintet state of the sandwich complex. This species is predicted to have essentially the same vibrational spectrum as the corresponding quintet ground state for the monobenzene complex, with two closely spaced modes (3087 and 3091 cm^{-1}) of similar intensity. Again, it is easily possible that such a doublet is present but not resolved within our line width. Indeed, the experiment finds spectra that are essentially identical for these two complexes. The occurrence of identical single-peak spectra can only be consistent with theory if both complexes are quintets. However, this can only be possible if density functional theory has grossly misjudged the relative energetics of the triplet and quintet spin states for the dibenzene complex.

Unfortunately, just such a problem with DFT is entirely possible, as this method is well-known to be problematic for open-shell systems.[47] Indeed, we previously found the same kind of problem for $V^+(C_6H_6)_{1,2}$ complexes in the lower frequency region, where the measured spectrum agreed with theory for the $n = 1$ complex but did not for the dibenzene complex.[13,15] At the very least, these combined IR spectra from the fingerprint region and the C−H stretch region call into serious question the ability of DFT to handle the correct spin state for these complexes. To investigate this problem further, we performed a single point MP2 calculation (6-311++G** basis)[15] on the $V^+(C_6H_6)_2$ complex at the geometry determined by DFT. At this structure, MP2 also favors the triplet species by a large energy difference (27.9 kcal/mol). It is therefore not clear at this point why there is apparent disagreement between experiment and theory in these spectra. DFT either misses the spin state or does not accurately predict the vibrational patterns in these states. This is clearly an issue that needs to be investigated more thoroughly with a variety of theoretical methods.

The spectrum for $V^+(C_6H_6)_2Ar$ has an additional weak band occurring at 3108 cm^{-1}. There are a few possibilities for assignment of this lower intensity band. The $^3B_{3g}$ species is predicted to have modes with higher frequencies than those of the $^5B_{2g}$ species. This band could therefore result from an additional minor population of triplet species in the beam. Another possibility is a combination band on the benzene itself or for the benzene in combination with an argon stretch. Calculations on complexes such as these that include the argon would be useful to assign this band and to provide further insight into the possibility of shifts it may introduce into these spectra.

Conclusion

We report here the first gas phase infrared spectra for $V^+(C_6H_6)_{1,2}Ar$ and $V^+(C_6H_6)_{3,4}$ complexes, which are also apparently the first IR data for metal ion−benzene complexes in the C−H stretching region. The smaller rare-gas tagged complexes yield simple spectra with one main band shifted to higher frequency than the C−H stretch of free benzene. Once the number of benzene ligands exceeds the coordination number of 2 a multiplet attributed to the Fermi triad of benzene is observed. This confirms that a stable core is established at $n = 2$ and subsequent benzene molecules act as solvent for this core sandwich complex. The C−H stretching mode measured for $V^+(C_6H_6)Ar$ agrees with the pattern of IR-active bands predicted in this region for the monobenzene complex in its $^5B_1$ state, which is predicted as one of the likely candidates for the ground state. However, the spectrum of the $V^+(C_6H_6)_2Ar$ complex exhibits systematic deviations from the spectrum predicted for the sandwich ion. Although the effects of argon cannot be completely excluded, it appears that the best assignment for the $V^+(C_6H_6)_2$ complex involves a quintet ground state rather than the triplet state predicted to be much more stable by DFT. These data are consistent with our previous IR measurements in the fingerprint region, which revealed the possible problems that DFT has in predicting the electronic spin state for these sandwich complexes.

Density functional theory is being applied widely to organometallic complexes, and further work is needed to explore the potential problems found here. These new IR measurements can be extended to other metal cation−benzene complexes. Systematic studies are underway to investigate trends in the vibrational shifts for different transition metal−benzene complexes and the details of the theory−experimental comparison for these systems.

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