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Photodissociation of $M^+(benzene)_x$ complexes (M = Ti, V, Ni) at 355 nm

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Abstract

Transition metal cation–benzene complexes of the form $M^+(C_6H_6)_{1–7}$ (M = Ti, V, Ni) are produced in a laser vaporization pulsed nozzle cluster source. The clusters are mass selected and photodissociated using the third harmonic of a Nd:YAG laser (355 nm). $Ti^+(C_6H_6)$ fragments via ligand decomposition to produce $Ti^+C_4H_2$, $Ti^+C_2H_2$, and Ti^+. $V^+(C_6H_6)$ fragments by ligand elimination of neutral benzene to give V^+ as the primary fragment. $Ni^+(C_6H_6)$ fragments via both ligand elimination and a photoinduced charge transfer pathway to give benzene cation. Complexes with two benzene ligands fragment by the loss of a single neutral benzene to leave $M^+(C_6H_6)$ as the fragment. Clusters with more than two benzenes fragment directly down to $M^+(C_6H_6)_2$ with a small amount of $M^+(C_6H_6)$ for M = Ti and Ni. This indicates that a stable sandwich core is established at $M^+(C_6H_6)_2$ that is solvated by subsequent benzenes. There is no evidence for three-fold coordination in any of these complexes.

Keywords: Clusters; Organometallic ions

1. 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 in the condensed phase [7,8]. Condensed phase complexes have been studied using infrared spectroscopy, and shifts in the ligand based vibrations give information on the metal–ligand interaction [9–12]. Until recently, such information has been limited for gas phase ion systems. However, we have recently reported the application of infrared photodissociation spectroscopy for a variety of gas phase transition metal ion–benzene complexes in the fingerprint region using a free electron laser [13–15]. In other new work, we reported IR photodissociation spectroscopy for $V^+(benzene)_x$ and $V^+(benzene)_xAr$ in the C–H stretch region using a tunable IR Optical Parametric Oscillator/Amplifier (OPO/OPA) laser system [16]. These new IR spectroscopy studies provide significant insight into the structures and binding interactions of metal ion–benzene complexes. UV photodissociation measurements complement these IR studies, providing a probe of bonding energetics and coordination numbers for such complexes [17]. This study focuses on the UV (355 nm) photodissociation of $M^+(C_6H_6)_{1–7}$ (M = Ti, V, Ni).

Many metal ion–benzene complexes have been studied in the gas phase by mass spectrometry [17–22]. Bond energies have been determined for such systems using collision-induced dissociation (CID) [19], equilibrium mass spectrometry [20] and UV–vis photodissociation [18]. Theory has investigated the structures and energetics of these systems [2,3,23–29]. Kaya and coworkers demonstrated that various metal–benzene complexes form multiple-decker sandwich structures of the form $M_x(benzene)_y$ where $y = x + 1$

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[21]. This tendency was most pronounced for earlier transition metal complexes, such as those containing vanadium or titanium. Later transition metals clustered in a different manner, forming "rice-ball" structures of metal clusters surrounded by benzene ligands. The multiple-decker sandwich structures were confirmed by ion mobility measurements performed by Bowers and coworkers [22]. Photoelectron spectroscopy has been applied to metal–benzene anions [21b,30]. Recently, an IR absorption spectrum was obtained for V^+(benzene)$_2$ that was size-selected as a cation then deposited and subsequently neutralized in a rare gas matrix [31]. Lisy and coworkers have obtained gas phase IR photodissociation spectra for alkali cation–(water)$_x$(benzene)$_y$ complexes in the O–H stretch region [32]. We have reported the vibrational spectra for several metal ion–benzene complexes in the 600–1700 cm^{-1} region [13–15]. These studies demonstrated systematic shifts in the ring based vibrations of these complexes [15]. A comprehensive comparison to density functional theory (DFT) calculations was also presented [15]. A recent communication showed that IR photodissociation spectroscopy could be applied to V^+(benzene)$_x$ and V^+(benzene)$_x$Ar complexes in the C–H stretch region [16].

UV and visible photodissociation studies have been performed previously by our group for many metal cation–ligand systems including M^+(benzene)$_x$ [17], $M^+(C_{60})_x$ [33,34], M^+(coronene)$_x$ [34–36], and M^+(cyclooctatetraene)$_x$ [37]. Yeh and coworkers have employed photodissociation to study the binding in a variety of related systems including $M^+(C_5H_5N)$ [38], M^+(furan) [39], and M^+(benzene) [40]. In many cases photodissociation occurs by simple ligand elimination in which an intact neutral ligand leaves the cluster and the metal cation or a smaller metal–ligand species is the charged fragment. In other cases ligand decomposition can occur, the metal complex loses smaller stable neutral fragments and a metal-containing ion is produced as a fragment. Yet another dissociation pathway is photoinduced charge transfer, as we have seen with several M^+(benzene)$_x$ systems [17]. Fragmentation of these complexes yields a charged organic and a neutral metal atom by either direct excitation into a charge transfer state at an energy above the dissociation limit or via an electronic curve crossing. For many metal ion–ligand systems, ligand elimination is expected based on the structural stability of the ligand studied. It is also interesting to see if a certain cluster size is produced as a common fragment from larger clusters. When this occurs, it is usually an indication that coordination around the metal ion is complete at this cluster size. In this way, the experiment helps to elucidate coordination numbers. The previous studies of $M^+(C_6H_6)$ performed by this group have focused on photoinduced charge transfer in complexes with only one benzene ligand [17]. The present study expands this earlier work to complexes with multiple benzene ligands.

2. Experimental section

The experimental apparatus has been described previously [41]. Clusters are produced via laser vaporization (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 [17] a free expansion of benzene seeded in Ar produces clusters of the form $M^+(C_6H_6)_x$. The molecular beam is skimmed from the source chamber into a differentially pumped mass spectrometer chamber. Cations are pulse accelerated into the first flight tube and mass selected by pulsed deflection plates located just prior to the reflection region. Each cluster size of interest is mass selected and photodissociated using the third harmonic (355 nm) of a Nd:YAG laser. The data are collected by a difference method, in which the mass spectrum with the fragmentation laser "off" is subtracted from that with it "on." This gives a negative-going parent peak due to depletion and positive-going fragment peaks. Parent and fragment ions are mass analyzed in the second flight tube and detected using an electron multiplier tube and a digital oscilloscope (LeCroy 9310A). Data is transferred to a PC via an IEEE-488 interface.

The laser pulse energy is varied for each complex studied. The normal setting employs the unfocused output of the laser at about 20 mJ/cm^2 pulse, while low power experiments go down to levels of about 1 mJ/cm^2 pulse.

3. Results and discussion

The mass spectra of clusters obtained for C_6H_6 with titanium, vanadium, and nickel are shown in Fig. 1. For all

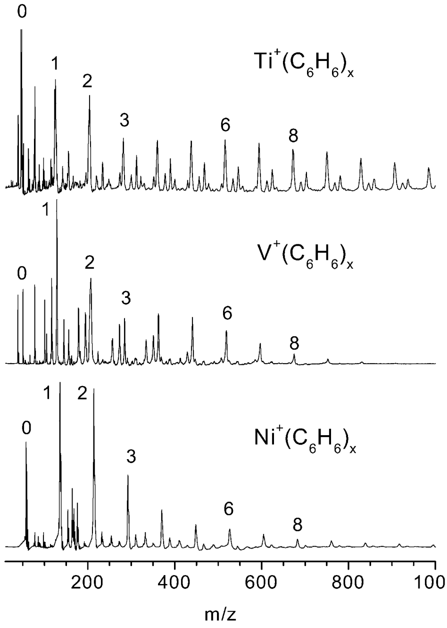

Fig. 1. Time-of-flight mass spectra for Ti–, V–, and Ni–$(C_6H_6)_x$ complexes formed in an Ar expansion.

three metals, the mass spectra consist predominately of metal ion–benzene adducts of the form $M^+(C_6H_6)_x$. Because metal atom recombination is limited in this particular cluster source configuration, multiple metal atom species, and in particular the multiple-decker sandwich or rice-ball clusters described by Kaya and coworkers [21], are not produced efficiently. Clustering is efficient out to 10 or more benzene ligands. After $n = 2$, however, a sharp drop off in intensity occurs for all three metal ion–benzene species. This could indicate particular stability for complexes with one or two benzene ligands. Other masses not associated with metal ion–benzene adducts are also present in all three mass spectra. For Ti^+, these masses are assigned as $K^+(C_6H_6)$, $Ti^+(H_2O)(C_6H_6)_x$, $(C_6H_6)_x{}^+$, and $Ti^+(C_6H_6)_xAr$. In the mass spectrum of $V^+(C_6H_6)_x$, the other masses are metal ion–benzene adducts of sodium and potassium. For Ni^+, the other mass peaks are assigned as $Ni^+(H_2O)(C_6H_6)_x$, $Ni^+(C_6H_6)_xAr$, and $Ni_2{}^+(C_6H_6)_x$.

The fragmentation difference mass spectra taken at 355 nm of the $M^+(C_6H_6)$ parent ions for M = Ti, V, and Ni are shown in Fig. 2. As mentioned earlier, three general types of photofragmentation can occur: ligand decomposition, ligand elimination, and photoinduced charge transfer. All three types of dissociation are observed in the fragmentation patterns of these selected transition metal cation–benzene complexes. As shown in the figure, the photodissociation of $Ti^+(C_6H_6)$ appears to follow three possible fragmentation pathways:

$$Ti^+(C_6H_6) \rightarrow Ti^+ + C_6H_6 \quad (1)$$

$$Ti^+(C_6H_6) \rightarrow Ti^+C_2H_2 + C_4H_4 \quad (2)$$

$$Ti^+(C_6H_6) \rightarrow Ti^+C_4H_2 + C_2H_4 \quad (3)$$

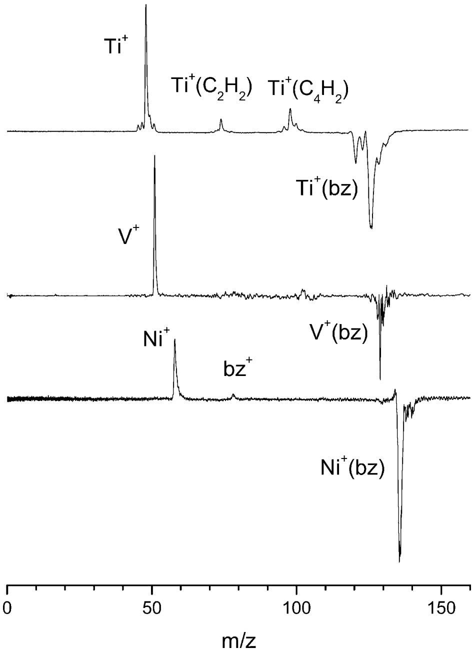

Fig. 2. Photofragmentation difference mass spectra of $M^+(C_6H_6)$ complexes at 355 nm where M = Ti, V, and Ni.

At first glance, it is not clear if the Ti^+ fragment occurs by ligand elimination from $Ti^+(C_6H_6)$ or by further fragmentation of $Ti^+(C_4H_2)$ or $Ti^+(C_2H_2)$. An examination of the thermodynamics of these pathways helps to explain which, if any, is energetically possible and whether or not these processes are single or multiphoton. For pathway number one, we can compare the bond energy of $Ti^+(C_6H_6)$ with the incident photon energy to see whether this process could be single or multiphoton. A table of metal ion–benzene bond energies derived from CID measurements is presented in Table 1. $Ti^+(C_6H_6)$ is bound by 61.9 kcal/mol (2.68 eV; $\sim$21,600 cm^{-1}) [19]. The incident photon energy at 355 nm is 3.49 eV or $\sim$28,200 cm^{-1}. This shows that the incident photon energy is enough to break this bond for simple ligand elimination. The ionization potential of titanium atom (6.82 eV) is less than that of benzene (9.24 eV), and therefore it makes sense that titanium is charged and the benzene is neutral in this ligand elimination process.

$Ti^+(C_6H_6)$ also undergoes ligand decomposition to give $Ti^+(C_4H_2)$ and $Ti^+(C_2H_2)$. This is somewhat surprising because of the high stability of benzene. However, titanium is extremely reactive and is known to undergo insertion chemistry with many small hydrocarbons [42–45]. On the other hand, Schwarz and coworkers found Ti^+ to be unreactive towards benzene [42]. Photoexcitation apparently provides the activation energy necessary for a reaction to occur here. The appearance of $Ti^+(C_2H_2)$ is not too surprising because $C_2H_2{}^+$ is a prominent fragment in the electron impact ionization (EI) mass spectrum of benzene [46]. Acetylene is also rather strongly bound to Ti^+ with a D_0 of 60.4 kcal/mol (2.62 eV) [40], so it is makes sense that this ion appears as a fragment. The formation of $Ti^+(C_4H_2)$, however, is intriguing. This could occur because ethylene, C_2H_4, is a relatively good neutral leaving group, or because the $Ti^+(C_4H_2)$ fragment has particular stability. In fact, diacetylene, $C_4H_2{}^+$, is also seen in large quantities in the EI mass spectrum of C_6H_6 [46]. It is possible that C_4H_2 takes the form of diacetylene when it complexes with Ti^+. Unfortunately, to our knowledge, theoretical or experimental bond energies for this complex are not known. Because the thermodynamics of these complexes has not been measured, it is not possible to evaluate the energetics of these ligand fragmentation processes.

Table 1
Metal ion–benzene bond energies (D_0; eV) determined by collision-induced dissociation [19b]

Complex	$x = 1$	$x = 2$
$Ti^+(C_6H_6)_x$	2.68	2.62
$V^+(C_6H_6)_x$	2.42	2.55
$Cr^+(C_6H_6)_x$	1.76	2.40
$Mn^+(C_6H_6)_x$	1.38	2.10
$Fe^+(C_6H_6)_x$	2.15	1.94
$Co^+(C_6H_6)_x$	2.65	1.73
$Ni^+(C_6H_6)_x$	2.52	1.52
$Cu^+(C_6H_6)_x$	2.26	1.61

The values shown are for the loss of one benzene ligand.

To examine the possible wavelength dependence of these fragmentation processes, we also used 532 nm light for photodissociation (data not shown). However, we observed the same fragments in about the same relative intensities at this wavelength. This is somewhat surprising. As described earlier, the metal–ligand bond energy of $Ti^+(C_6H_6)$ is 2.68 eV ($\sim$21,600 cm^{-1}). When the photodissociation wavelength is 355 nm ($\sim$28,200 cm^{-1}), the incident photon energy is greater than the bond energy. However, this is not the case for excitation at 532 nm ($\sim$18,800 cm^{-1}). Although multiphoton processes cannot be completely ruled out, the overall signal intensity is large and the power dependence seems to indicate a single-photon process. This discrepancy can be accounted for if a fraction of the $Ti^+(C_6H_6)$ complexes present in the beam is in a metastable excited state. Previous DFT calculations [15] found that $Ti^+(C_6H_6)$ has a $^4A_1$ ground state with a low-lying excited $^2A_2$ state some 0.42 eV ($\sim$3400 cm^{-1}) higher in energy. If some ions in our experiment are produced by the laser plasma in an excited doublet state of the complex, then decomposition is a much lower energy process, and excitation at 532 nm can access the ligand elimination channel. It is well documented that laser vaporization sources can produce metastable excited states for transition metal species [47–50], and so the production of such metastable complexes is not too surprising. The presence of a small fraction of an excited metastable state could also influence the ligand decomposition pathways seen here, as it is well known that the reactivities of metal ions are highly dependent on their electronic state [47–50]. In fact, for Ti^+ the first doublet excited state is known to be over 100 times more reactive towards certain hydrocarbons than the quartet ground state [49].

Fig. 2 also shows the photofragmentation of $V^+(C_6H_6)$ at 355 nm. This pattern is much simpler than that of $Ti^+(C_6H_6)$. As shown, $V^+(C_6H_6)$ fragments by simple ligand elimination of a whole neutral benzene ligand. These results are consistent with those previously presented by Yeh and coworkers for $V^+(C_6H_6)$ using both 532 and 355 nm light [40]. The binding energy of $V^+(C_6H_6)$ (55.9 kcal/mol; 2.42 eV) [19] is slightly less than that of $Ti^+(C_6H_6)$, and this process likely takes place via single-photon absorption. The ionization potential of vanadium (6.74 eV) is also much less than that of benzene, consistent with the production of the charged metal fragment. Because no ligand decomposition is observed, it is tempting to say that V^+ is less reactive towards benzene than Ti^+. This trend has been observed previously in experiments that produce metal-carbide clusters [45,46]. In those experiments, Ti and V ablated in the presence of small hydrocarbons react by insertion into C–H bonds followed by hydrogen elimination, forming the stable metal-carbide clusters. This process is much more efficient for titanium than it is for vanadium. Similar results have been found in reaction studies using several different hydrocarbons, all indicating that Ti^+ is more reactive than V^+ [42,43].

The photofragmentation of $Ni^+(C_6H_6)$ at 355 nm is also shown in Fig. 2. This complex dissociates in two parallel pathways, simple ligand elimination and photoinduced charge transfer. $Ni^+(C_6H_6)$ is bound by 58.1 kcal/mol (2.52 eV) [19], which is less than the incident photon energy (3.49 eV), and so the ligand elimination can occur by a one-photon process. The IP of nickel (7.64 eV) is less than that of benzene, consistent with the production of Ni^+ as the charged fragment. However, the charge transfer process is somewhat surprising. As reported earlier by this group [17], when charge transfer photodissociation occurs, an upper limit can be placed on the metal ion–ligand bond energy according to the following equation:

$$D_0 \leq h\nu - \Delta\mathrm{IP}$$

where $h\nu$ is the incident photon energy and ΔIP the difference in the ionization potentials between the metal and the ligand. In the case of $Ni^+(C_6H_6)$, with ΔIP equal to 9.24–7.64 = 1.60 eV, an upper limit of $D_0 \sim 1.89$ eV can be derived for excitation at 355 nm. Surprisingly, this is much less than the experimental bond energy (2.52 eV) determined previously for this system [19]. It is possible that this fragmentation channel is caused by a multiphoton process, but it is observed at our lowest laser fluences, suggesting that this is not the case. Again, another possibility is that there is a small fraction of $Ni^+(C_6H_6)$ in the molecular beam that is trapped in a metastable excited state. Ni^+ has a ^2D ground state with a spin-forbidden ^4F state lying about 1 eV higher in energy [46]. The difference between the CID bond energy and the upper limit on the dissociation energy suggested above is approximately equal to this value (0.92 eV). The charge transfer channel seen here is then probably due to photoexcitation of a metastable excited state in the complex that correlates to this quartet atomic state, which then makes it possible to access the charge transfer potential with a lower energy photon.

It is interesting to investigate the fragmentation pattern of these complexes when more than one ligand is attached. The photofragmentation mass spectra at 355 nm for $M^+(C_6H_6)_2$ complexes (M = Ti, V, Ni) are shown in Fig. 3. As shown, all three complexes fragment primarily by the loss of a single neutral benzene ligand. A very small amount of further fragmentation is seen for $Ti^+(C_6H_6)_2$ and $Ni^+(C_6H_6)_2$, but this is attributed to a small amount of multiphoton absorption (the smaller fragments are not present at our lowest laser powers). The energetics of benzene elimination from these sandwich complexes have been measured by CID experiments, and these values are presented in Table 1 [19]. In each case, the incident photon energy (355 nm, 3.49 eV) exceeds the binding energy of the second ligand, and therefore the loss of a benzene unit is not surprising. The same results were reported for $V^+(C_6H_6)_2$ by Yeh and coworkers [40].

Transition metal ion–benzene complexes are usually expected to have a coordination number of two, as in the familiar sandwich structures. However, the rice-ball structures proposed by Kaya and coworkers [21] for larger multimetal–benzene clusters suggest that some late transition metals might have coordination numbers of three or more. Thus, it is interesting to study the photofragmentation

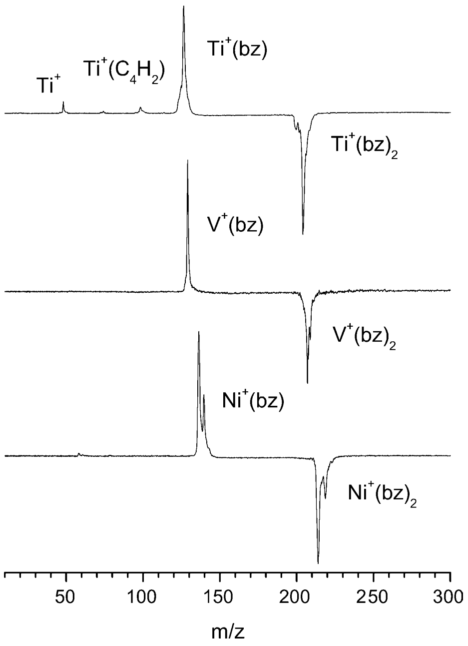

Fig. 3. Photofragmentation difference mass spectra of $M^+(C_6H_6)_2$ complexes at 355 nm where M = Ti, V, and Ni.

behavior of larger $M^+(C_6H_6)_x$ ($x \geq 2$) complexes. As more benzene is attached to the cluster, at some point it will not be able to make direct contact with the metal cation because coordination is complete. The external benzene molecules will attach to the “core” benzene ligands and pile up on the outside of the cluster, acting essentially as solvent species. Because they are bound primarily by van der Waals forces, the binding energies of the external ligands would approximate that of a neutral benzene dimer ($\sim$1000 cm^{-1}) [51–53]. Therefore, for clusters up to very large sizes, the 355 nm photon energy of 28,200 cm^{-1} used here should be enough to evaporate all of these solvent ligands and leave only the stable core behind.

The photodissociation measurements on several of the larger metal ion–benzene complexes are shown in Figs. 4–6 for each of the three metal ions. In all three systems, benzene molecules evaporate down to the $M^+(C_6H_6)_2$ complex, as expected for bis-benzene sandwiches. For Ti and Ni, a significant amount of $M^+(C_6H_6)$ is also produced at smaller cluster sizes, but this channel is progressively less intense for the larger clusters. This is most likely due to multiphoton effects in which subsequent fragmentation of the sandwich core occurs, as these fragments are not observed at lower laser fluences. These results clearly demonstrate that coordination for these metal ion–benzene complexes is complete at two. Additional ligands solvate this stable sandwich core. None of the complexes show any evidence for coordination numbers larger than two. Our group has recently studied $Ni^+(acetylene)_x$ complexes by infrared photodissociation. These measurements found a coordination number of four acetylenes for Ni^+ in that system [54], while similar measurements found a coordination number of three acetylenes in the $Co^+(C_2H_2)_x$ complexes (R.S. Walters, M.A. Duncan, unpublished work). Different coordination numbers are clearly possible for other ligands, but it remains to be seen if there will be any coordination other than two for metal ion–benzene complexes.

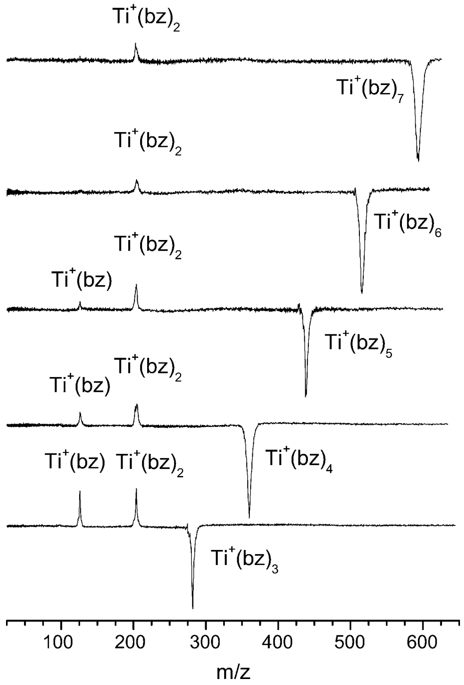

Fig. 4. Photofragmentation difference mass spectra of $Ti^+(C_6H_6)_{3–7}$ complexes at 355 nm.

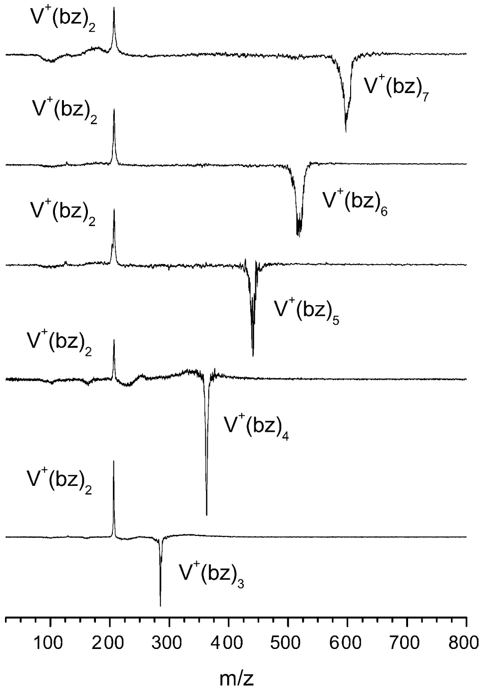

Fig. 5. Photofragmentation difference mass spectra of $V^+(C_6H_6)_{3–7}$ complexes at 355 nm.

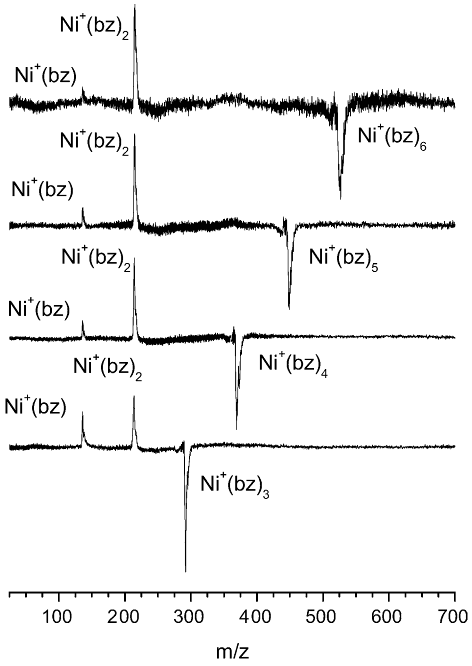

Fig. 6. Photofragmentation difference mass spectra of $Ni^+(C_6H_6)_{3-6}$ complexes at 355 nm.

4. Conclusions

Titanium, vanadium, and nickel metal ion–benzene systems have been studied using fixed frequency photodissociation at 355 nm. $Ti^+(C_6H_6)$ fragments by ligand elimination and ligand decomposition while $V^+(C_6H_6)$ and $Ni^+(C_6H_6)$ fragment by simple ligand elimination. There is evidence in the dissociation mass spectra for $Ti^+(C_6H_6)$ and $Ni^+(C_6H_6)$ that metastable excited states are present in the molecular beam. For Ti^+(benzene), this explains the unexpected dissociation at 532 nm, while for $Ni^+(C_6H_6)$ it leads to an unexpected charge transfer dissociation. These data reinforce earlier findings that such metastable excited states can have a strong influence on transition metal ion chemistry, and that the presence of such states can confuse measurements of complex energetics.

Complexes with two benzene ligands fragment via the loss of a single benzene unit, consistent with the known bonding energetics for these species. Complexes with more than two benzene ligands fragment by multi-ligand elimination, forming the respective $M^+(C_6H_6)_2$ sandwich ion as the terminal photofragment. This confirms the expected coordination of two for these metals. There is no evidence for complexes with a coordination number greater than two.

Acknowledgment

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