Infrared Spectra of Gas-Phase V⁺−(Benzene) and V⁺−(Benzene)₂ Complexes

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Metal−benzene ions have a special attraction because of their relevance for catalysis and biological processes,[1,2] and for the importance of aromatic π-bonding to organometallic chemistry.[3,4] These complexes are also interesting because they form sandwich structures. Gas-phase complexes can in principle be compared to those produced by conventional synthesis. Unfortunately, there are few studies of spectroscopy that provide insight into the structures and bonding of these species. Infrared (IR) spectroscopy has been applied to condensed-phase complexes,[3,4] but such measurements have not been possible in the gas phase. We report here a new method for the study of the IR spectroscopy of mass-selected metal ion complexes. The results for vanadium−benzene provide the first IR spectroscopy for transition metal ion−benzene complexes in the gas phase.

Metal−benzene sandwiches, including bis-benzene vanadium, are familiar in the condensed phase[3,4] and in gas-phase ion chemistry.[5−15] As shown by Kaya, gas-phase $V_x(benzene)_y$ complexes form multiple-decker sandwiches.[8] Bowers probed these complexes with ion mobility measurements.[9] Kaya 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.[10] Lisy has measured IR spectra of alkali cation−benzene complexes,[11] but there are no vibrational spectra for any ionized transition metal complex with benzene. Low ion densities and poor IR sources have precluded such studies.

In this work, $V(C_6H_6)_{1,2}$ complexes are produced in a molecular beam by laser vaporization.[6] Neutral complexes enter an ion trap mass spectrometer,[16] where they are ionized with an ArF excimer laser (193 nm; 6.42 eV). Efficient one-photon ionization occurs for both complexes at this wavelength.[8] The cations are trapped for milliseconds, and isolated by mass with the RF potentials of the trap. Tunable IR excitation is accomplished with the Free Electron Laser for Infrared eXperiments (FELIX)[17] that produces intense 10−50 mJ pulses in the 600−1800 cm⁻¹ region of this experiment. After IR excitation, the contents of the ion trap are extracted into a time-of-flight spectrometer for mass analysis.[16] Resonance enhanced multiphoton dissociation (IR-REMPD) produces the V⁺ and V⁺(C₆H₆) photofragments from V⁺(C₆H₆) and V⁺(C₆H₆)₂, respectively. These ions are recorded as a function of wavelength to obtain IR spectra. From the known bond energies of V⁺(C₆H₆) (55.8 kcal/mol; ~19 500 cm⁻¹) and V⁺(C₆H₆)₂ (58.8 kcal/mol; ~20 600 cm⁻¹),[7] it is clear that dissociation is a

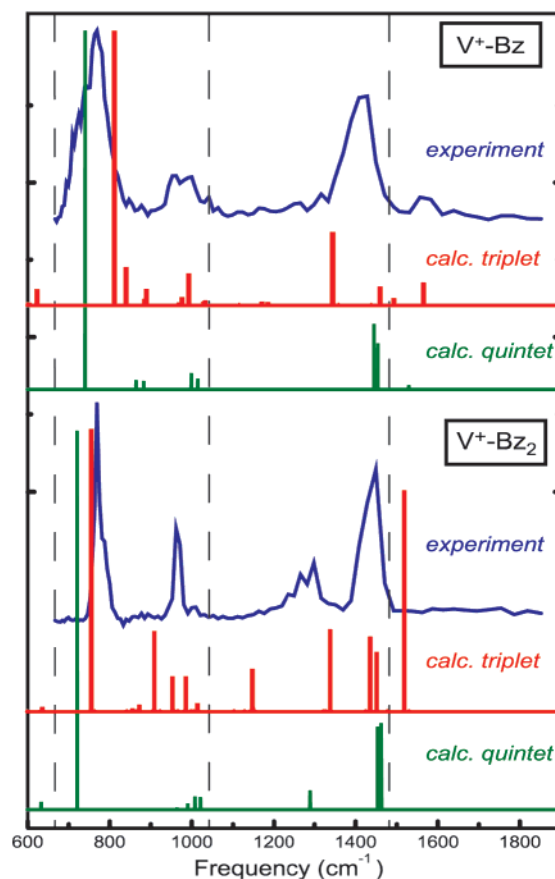**Figure 1.** The IR-REMPD spectra of V⁺−(benzene)₁,₂ ions. Dashed lines show the positions of free benzene vibrations, while the solid lines show the spectra calculated with DFT in the quintet and triplet electronic states.

multiphoton process. However, multiphoton processes involving 100 or more photons have been seen before with FELIX.[18,19]

The IR spectra obtained for V⁺(C₆H₆) and V⁺(C₆H₆)₂ are shown in Figure 1, and the band positions are given in Table 1. Strong bands near 700 and 1400 cm⁻¹ and weaker bands near 1000 cm⁻¹ are measured for both complexes. V⁺(C₆H₆) has a weaker band near 1600 cm⁻¹ and V⁺(C₆H₆)₂ has a broad band near 1300 cm⁻¹. The laser is much narrower than these line widths, which are broader for V⁺(C₆H₆) than for V⁺(C₆H₆)₂. Line widths also vary from band-to-band for the same molecule. The line widths arise from the thermal populations produced by ionization and the dynamics of multiphoton excitation.[18] By comparison with previous spectra of metal−benzene complexes in the condensed phase,[4,5] the bands are

Table 1. Vibrations Measured and Calculated for V$^+$−(benzene) and V$^+$−(benzene)$_2$ and Their Comparison to Previous Experiments and Theory

vibrational mode	C$_6$H$_6$ gas phase	V$^+$(C$_6$H$_6$) this work	V$^+$(C$_6$H$_6$) theory (quintet)	V(C$_6$H$_6$)$_2$ condensed phase	V(C$_6$H$_6$)$_2$ theory (doublet)	V$^+$(C$_6$H$_6$)$_2$ this work	V$^+$(C$_6$H$_6$)$_2$ theory (quintet)	V$^+$(C$_6$H$_6$)$_2$ theory (triplet)
ν_{11} out-of-plane C−H bend	673	769	744	742	742	769	722	757
ν_1 ring breathing	992			957	948	962	965 vw	954
ν_{18} in-plane C−H bend	1038	980	1000/1016	990	985	1008	1008	987/1016
ν_{19} in-plane C ring dist.	1486	1425	1447/1458	1415		1449	1455/1464	1438/1454
ν_8 sym in-plane C−H bend	1596	1565	1531				1457 vw	1521

recognized as those of the benzene molecule perturbed by the metal bonding. Table 1 compares these band positions to those of free benzene,[20] the known neutral V−(C$_6$H$_6$)$_2$ complex,[3,4] and the predictions of theory. The bands at 769 cm^{-1} for both complexes are assigned to the ν_{11} mode of benzene (out-of-plane H bend), which is blue-shifted from that of free benzene. Bands near 1000 cm^{-1} correspond to the ν_{18} mode (in-plane C−H bend), which is red-shifted with respect to free benzene. Strong ν_{19} bands occur at 1425 and 1449 for V$^+$(C$_6$H$_6$) and V$^+$(C$_6$H$_6$)$_2$, respectively (in-plane C ring distortion), which are also red shifted. ν_8 is not IR active in free benzene, but it becomes active in the complexes. All the bands are red-shifted with respect to those of free benzene except the ν_{11} bands, which have significant blue shifts. These same trends are seen for the vibrational spectra of condensed-phase metal−benzene complexes.[4,5] The metal withdraws electron density from the π orbitals, thus weakening the bonding of the ring system and making the ring-based vibrations less rigid. The out-of-plane C−H bend (ν_{11}) shifts to higher frequency because of the added metal repulsion near the turning points of this vibration. The V$^+$(C$_6$H$_6$)$_2$ cation has smaller shifts than its neutral counterpart for the ν_{19} mode, but larger shifts for ν_{18} and ν_{11}.

Electronic structure calculations are performed with Gaussian 98[21] using density functional theory with the hybrid B3LYP functional. The standard 6-31G* basis set is employed for benzene, while the metal is represented by a polarized triple-ζ basis.[12] This level of theory provides excellent results for the known V(C$_6$H$_6$)$_2$ neutral complex. Calculations predict a quintet ground state for V$^+$-(C$_6$H$_6$), as for V$^+$[^{5}D (d^4)], with a triplet state lying only 5 kcal/mol higher. A spin change occurs with the addition of the second benzene, producing a triplet V$^+$(C$_6$H$_6$)$_2$ lying 25.7 kcal/mol lower than the quintet. This leads to a second benzene more bound than the first (62.6 vs 54.6 kcal/mol) in agreement with experiment.[7] A similar spin change is found in other V$^+$ complexes,[22] driven by reduced metal−ligand repulsion and increased metal-to-ligand back-donation.[12] The V$^+$ electronic configuration in the ideal C_{6v} V$^+$-(C$_6$H$_6$) is a$_{1g}^1$e$_1^2$e$_2^1$ (a$_{1g}^1$e$_1^3$e$_2^0$) for a quintet (triplet) spin state. Jahn−Teller deformation occurs, leading to ^{5}B$_2$ and ^{3}A$_2$ boat-shaped C_{2v} structures. Similar distortions occur from an ideal D_{6h} V$^+$(C$_6$H$_6$)$_2$ for both the quintet (a$_{1g}^1$e$_{1g}^2$e$_{2g}^1$) and the triplet (a$_{1g}^1$e$_{1g}^3$e$_{2g}^0$) spin states, leading to D_{2h} structures and ^{5}B$_{2g}$ and ^{3}B$_{3g}$ states, respectively. The vibrational bands predicted for both complexes in the triplet and quintet electronic states are shown below each spectrum in the figure. The frequencies are reduced by 3.1%, to correct the free benzene modes calculated at the same level. There is a good match for the quintet state with the observed V$^+$(C$_6$H$_6$) bands, but the shifts relative to free benzene are underestimated for the strong ν_{11} and ν_{19} bands. In the triplet state predicted for V$^+$(C$_6$H$_6$)$_2$, the ν_{11} band agreement is good, but strong ν_{16} and ν_{17} bands are predicted near 1149 and 1521 cm^{-1} where nothing is observed. The quintet state matches the spectrum better, although it is calculated to lie at a much higher energy. It is conceivable that the ionization process produces complexes that are not in their ground electronic state. The IR-REMPD detection scheme may also be selective for electronically excited species, as these have lower effective dissociation energies. Furthermore, it is possible that DFT fails in some unexplained way to treat the spin configuration for V$^+$(C$_6$H$_6$)$_2$. However, now that vibrational spectra can be measured, investigations into these previously unexplored questions can begin.

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