Photoelectron spectroscopy of titanium–benzene cluster anions

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Abstract

(Titanium)\textsubscript{n} (benzene)\textsubscript{m}\textsuperscript{−} cluster anions were studied by both mass spectrometry and anion photoelectron spectroscopy. The cluster anion series, Ti\textsubscript{n}(Bz)\textsubscript{m+1} (n = 1–6) dominated the mass spectra. Vertical detachment energies and adiabatic electron affinities were determined for (n,m) = (1,1), (1,2), (2,3), (3,4), (4,5), and (2,4). The evidence suggests that members of the Ti\textsubscript{n}(Bz)\textsubscript{m+1} series have multiple-decker sandwich structures. Ti\textsubscript{2}(Bz)\textsubscript{2} was observed and appears to be the dimer anion, (Ti(Bz))\textsubscript{2}−.

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1. Introduction

Metal–benzene complexes have been studied in the gas phase for over two decades. Armentrout and coworkers [1,2] studied M\textsuperscript{+}–Bz\textsubscript{2} (M = Ti–Cu, Ag; Bz = benzene) via collision-induced dissociation experiments. Duncan and coworkers [3] conducted photodissociation studies of M\textsuperscript{+}–Bz (M = Fe, Mg, Ag and Bi). Bowers and coworkers [4] investigated vanadium/benzene cation clusters using ion mobility spectrometry. Nakajima and coworkers [5–7] performed mass spectrometric and photoionization studies on M–Bz clusters and their cations (M = Sc–Cu) as well as photoelectron studies of vanadium–arene anion complexes. Eberhardt and coworkers [8] carried out photoelectron studies of M\textsubscript{2}Bz\textsuperscript{−} (M = Pt, Pd, Pb) cluster anions. Our group conducted photoelectron spectroscopy studies of M\textsubscript{n}(Bz)\textsubscript{m}− (M = Co, Fe, Ni) and on Co\textsubscript{n}(pyridine)\textsubscript{m}− cluster anions [9–11]. Broyer and coworkers [12] measured the electric dipole moment of MBz\textsubscript{2} (M = Sc, Ti, V, Co, Ni, Nb, Ta, and Zr) complexes.

In addition, several theoretical calculations have been conducted. Binding energies and geometries of transition metal cation–benzene complexes have been calculated by Bauschlicher et al. [13], by Koch and coworkers [14], by Chaquin et al. [15], and by Rao and coworkers [16]. Geometric structures of neutral transition metal–benzene complexes were investigated by Froudakis et al. [17], Rao and coworkers [16], and Yabushita and coworkers [18], while Pandey and coworkers [19] explored the magnetic moments for such systems. Anions of transition metal–benzene complexes have been studied extensively by Rao and coworkers [16,20,21].

Experimental and theoretical studies of titanium–benzene complexes have been relatively few in number. Experimental studies by Armentrout [1], by Nakajima and Kaya [5] and by Broyer and coworkers [12] have investigated neutral and cationic titanium–benzene clusters. Theory has considered neutral [15,16,18,19], cationic [15,16], and anionic [16] charge states of titanium–benzene clusters. The calculations by Rao and coworkers [16] on Ti(Bz)\textsuperscript{−} and Ti(Bz)\textsubscript{2}− cluster anions are of particular relevance to the present work. Here, we report our mass spectrometric and photoelectron spectroscopic study of titanium–benzene cluster anions.

2. Experimental

Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected beam of anions with
a fixed frequency photon source and energy analyzing the resultant photodetached electrons. This technique is governed by the energy-conserving relationship \( hv = E_{KE} + E_{BE} \), where \( hv \) is the photon energy, \( E_{KE} \) is the measured electron kinetic energy, and \( E_{BE} \) is the electron binding energy. The details of our apparatus have been described elsewhere [22]. Briefly, both mass spectra and anion photoelectron (photodetachment) spectra were collected on an apparatus consisting of a laser vaporization source, a linear time-of-flight mass spectrometer for mass analysis and selection, and a magnetic bottle photoelectron spectrometer for electron energy analysis. (The instrumental resolution is \( \sim 35 \text{ meV at 1 eV EKE.} \) The third harmonic (355 nm, 3.493 eV) of a Nd:YAG laser was used to photodetach the cluster anions of interest. Photoelectron spectra were calibrated against the atomic lines of Cu\(^+\).

Titanium–benzene cluster anions were generated in a laser vaporization source. A rotating, translating titanium rod (1/4 in. diameter, ESPI Company, 2N5 purity) was utilized as target in the laser vaporization source. It was ablated with the second harmonic (532 nm, 2.33 eV) of another pulsed Nd:YAG laser using approximately 10 mJ of power per pulse. Helium gas at \( \sim 4 \text{ atm, seeded with benzene vapor, was expanded through a pulsed valve into the source, thus generating and cooling the resultant titanium–benzene cluster anions.} \)

### 3. Results

A typical mass spectrum of titanium–benzene cluster anions is presented in Fig. 1. Due to titanium's five naturally-occurring isotopes, the mass spectrum of titanium–benzene cluster anions is relatively complex. Because our apparatus has unit mass resolution up to about 500, however, this does not present a serious problem. This allows us to distinguish all of the mass peaks belonging to titanium–benzene cluster anions up to sizes as large as such as Ti\(_3\)(Bz)\(_4\). The combination of unit mass resolution and careful attention to the isotopic peak–height ratios in a given species profile insured that we avoided cluster anions which had lost hydrogen atoms due to dissociative attachment of electrons to the benzene moiety. The main series of titanium–benzene cluster anions seen in our mass spectra is that of Ti\(_n\)(Bz)\(_n^+\) (\( n = 1–6 \)), although significant intensities of Ti\(_3\)(Bz)\(_2^-\) and Ti\(_2\)(Bz)\(_4^-\) are also seen routinely. Less often and under different source conditions, we also observed Ti\(_1\)(Bz)\(_1^-\). In the mass spectral/photoionization study by Kaya and coworkers [5], the most intense species observed was Ti\(_4\)(Bz)\(_7^+\).

The photoelectron spectrum of the Ti\(_1\)(Bz)\(_1^-\) cluster anion is presented in Fig. 2, followed by the photoelectron spectra of Ti\(_n\)(Bz)\(_n^+\) (\( n = 1–4 \)) cluster anions in Fig. 3 and the comparative photoelectron spectra of Ti(Bz)\(_2^-\) and Ti\(_2\)(Bz)\(_4^-\) in Fig. 4. Each of these spectra depict transitions from the electronic ground state of that particular cluster anion to the electronic ground state and energetically-accessible, excited states of its corresponding neutral cluster. The peaks are broadened by the vibrational/rotational manifold associated with each electronic state. The lowest EBE peak in each spectrum corresponds to the transition from the ground state of that cluster anion to the ground state of its corresponding neutral cluster. The EBE of the peak maximum is the vertical detachment energy, VDE. If there are no vibrational hot bands present, the EBE of the onset of electron intensity corresponds to the adiabatic electron affinity, \( EA_a \), of the neutral cluster. Since the cluster anions have internal energy corresponding to a significant temperature, however, the EBE that designates the \( EA_a \) value is typically interpreted as lying

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**Fig. 1.** A typical mass spectrum showing the Ti\(_n\)(Bz)\(_m^-\) cluster anions studied in this work.

**Fig. 2.** The photoelectron spectrum of Ti\(_1\)(Bz)\(_1^-\) recorded with 355 nm photons.
between the signal onset and the peak maximum. (We estimate the temperature of these cluster anions to be \( \sim 200 \) °C.) When the structure of the anion and its neutral are very similar, this peak is narrow. Under these circumstances, \( E_{Aa} \) is approximately equal to \( VDE \).

Table 1 summaries the \( VDE \) and \( E_{Aa} \) values of the cluster systems studied here.

### 4. Discussion

#### 4.1. \( Ti_1(Bz)_j^- \)

Pandey et al. [16] calculated the adiabatic electron affinity for \( Ti_1(Bz)_1 \) to be \( 0.7 \) eV. The \( E_{Aa} \) value for \( Ti_1(Bz)_1 \) derived from our measurements is \( 0.85 \pm 0.15 \) eV (see Table 1 and Fig. 2), in accord with their theoretical prediction. This \( E_{Aa} \) value is the transition energy between the electronic ground state of \( Ti_1(Bz)_1^- \) and the electronic ground state of \( Ti_1(Bz)_1 \) neutral. Agreement between the theoretically predicted and the experimentally measured value of this electronic transition energy suggests that the calculation has properly computed the spin multiplicities of these states. The calculation predicts the spin multiplicity of neutral \( Ti_1(Bz)_1 \) to be 5. Since the spin magnetic moment, in units of Bohr magnetons (\( \mu_B \)), is the spin multiplicity minus one, and since orbital magnetic moment contributions are thought to be small in clusters, this implies that the total magnetic moment of \( Ti_1(Bz)_1 \) is essentially \( 4 \mu_B \) per atom. Because the spin multiplicity for the Ti atom is 3, its magnetic moment is \( 2 \mu_B \). Thus, complexing a titanium atom with a benzene molecule doubles the...
magnetic moment, showing how sensitive magnetic properties are to their immediate environments.

4.2. Tiₙ/Bz/C₀⁻/ₙ+1

In examining the titanium–benzene cluster series, Tiₙ(Bz)ₙ/C₀⁻/ₙ+1, n = 1–4, one sees similarities among them which hint at their gross structures. Our experiments provided two sources of information, these being mass spectra and photoelectron spectra. The fact that the Tiₙ(Bz)ₙ/C₀⁻/ₙ+1 series dominates the observed mass spectrum (see Fig. 1) is itself suggestive of alternating, multi-decker sandwich structures, in which each titanium atom is located between two parallel benzene rings. This interpretation coincides with earlier conclusions about the structures of neutral transition metal/benzene clusters which were drawn by Nakajima and coworkers [5] based on their mass spectral data.

Our photoelectron spectra of Ti(Bz)₂, Ti₂(Bz)₃, Ti₁(Bz)₂ and Ti₄(Bz)₈ are also consistent with this sandwich motif. In Fig. 3, one sees a gradual shift and evolution of Tiₙ(Bz)ₙ/C₀⁻/ₙ+1 spectral profiles with increasing n, suggesting a sequential extension of the previous structure rather than a drastic structural change as one more titanium atom and one more benzene molecule are added to build the next member of the series, e.g., in going from Ti₄(Bz)₇ to Ti₅(Bz)₆⁻. (Table 1 shows the same gradual change as EAₙ values for this series increase with cluster size.) In an alternative motif, homogeneous titanium cluster anion cores could be imagined to be solvated by benzene molecules. However, when our Tiₙ(Bz)ₙ/C₀⁻/ₙ+1 spectra are compared with those of Tiₙ/C₀⁻/ₙ+1 recorded by Wang and coworkers [23], no significant similarity in profiles was seen, indicating that homogeneous titanium cluster anion moieties are not present in the Tiₙ(Bz)ₙ/C₀⁻/ₙ+1 series. Thus, the series shown in Fig. 3 should not be characterized as solvated, metal cluster anions.

We now consider each member of this series individually. The photoelectron spectrum of Ti(Bz)₂ has three major peaks, these being centered at 0.23, 1.05 and 1.40 eV. While broadened and shifted to higher EBE values, this pattern of transitions is similar to that of the atomic transitions seen by Feigerle et al. [24] in their photoelectron spectrum of the Ti⁺ anion. There, they found three major peaks centered at 0.080, 0.90 and 1.54 eV. We suggest that the photoelectron spectrum of Ti(Bz)₂ should be characterized as the photoelectron spectrum of Ti⁺, modified by the crystal field effects of two benzene molecules. Calculations [18] found the structures of Ti(Bz)₂ and Ti(Bz)₂/C₀⁻/₃ to be sandwich structures with Dₙₙₙ symmetry. Consistent with the proposed sandwich structure, dipole moment measurements [12] found neutral Ti(Bz)₂ to have a dipole moment of zero. Sandwich structures for Ti(Bz)₂ and Ti(Bz)₂/C₀⁻/₃, viz., |, appear to be well-supported by experiments and theory.

The theoretical prediction [16] for the electron affinity of Ti(Bz)₂, however, does not agree with our experimental results, cf., +0.18 eV (expt.) vs. −0.37 eV (theo.).

The photoelectron spectrum of Ti₂(Bz)₃ also displays three major features. While the spacings in this spectrum are not identical with those in the Ti(Bz)₂ spectrum, there is nevertheless, considerable similarity. We interpret this spectrum as reflecting the sequential growth of Ti₂(Bz)₃’s sandwich structure into a double-layer sandwich structure for Ti₂(Bz)₅, viz., ||. While the photoelectron spectrum of Ti₃(Bz)₄ is considerably broader than the spectrum of Ti₂(Bz)₃, we also interpret it as reflecting the sequential structural evolution from Ti₂(Bz)₅ to Ti₂(Bz)₇ to Ti₂(Bz)₉. We propose that Ti₃(Bz)₄ is a triple-layer sandwich structure, viz., ||||. Due to its high density of states, there are no distinguishable features in the photoelectron spectrum of Ti₄(Bz)₅. Nevertheless, an evolved similarity with the spectrum of Ti₃(Bz)₄ can be discerned, if one looks at the series as a whole. We speculate that the structure of Ti₄(Bz)₅ is a quadruple-layer sandwich structure, viz., |||||. All of the clusters in this series appear to have alternating, multiple-decker sandwich structures.

4.3. Ti₃(Bz)₄/C₀⁻/₃ vs. Ti(Bz)₂/C₀⁻/₃

Fig. 4 compares the photoelectron spectra of Ti₃(Bz)₄/C₀⁻/₃ and Ti(Bz)₂/C₀⁻/₃. The photoelectron spectrum of Ti₃(Bz)₄/C₀⁻/₃ is characterized by a sharp feature at EBE = 0.47 eV and two broad features centered at EBE = 1.6 and 2.4 eV. The spectral profiles of Ti₃(Bz)₄/C₀⁻/₃ and Ti(Bz)₂/C₀⁻/₃ are quite similar, although the spectrum of Ti₃(Bz)₄/C₀⁻/₃ has shifted to slightly higher EBE. We propose that Ti₃(Bz)₄/C₀⁻/₃ is the anion of the Ti(Bz)₂ dimer. The fact that the two Ti(Bz)₂ units remain intact within the dimer suggests that Ti(Bz)₂ is a very stable species.

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