

# Photoelectron spectroscopy of titanium–benzene cluster anions

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## Abstract

(Titanium)<sub>n</sub>(benzene)<sub>m</sub><sup>−</sup> cluster anions were studied by both mass spectrometry and anion photoelectron spectroscopy. The cluster anion series, Ti<sub>n</sub>(Bz)<sub>n+1</sub><sup>−</sup> (*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<sub>n</sub>(Bz)<sub>n+1</sub><sup>−</sup> series have multiple-decker sandwich structures. Ti<sub>2</sub>(Bz)<sub>4</sub><sup>−</sup> was observed and appears to be the dimer anion, (Ti(Bz)<sub>2</sub>)<sub>2</sub><sup>−</sup>.

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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<sup>+</sup>–Bz<sub>2</sub> (M = Ti–Cu, Ag; Bz = benzene) via collision-induced dissociation experiments. Duncan and coworkers [3] conducted photodissociation studies of M<sup>+</sup>–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<sub>2</sub>Bz<sup>−</sup> (M = Pt, Pd, Pb) cluster anions. Our group conducted photoelectron spectroscopy studies of M<sub>n</sub>(Bz)<sub>m</sub><sup>−</sup> (M = Co, Fe, Ni) and on Co<sub>n</sub>(pyridine)<sub>m</sub><sup>−</sup> cluster anions [9–11]. Broyer and coworkers [12] measured the electric dipole moment of MBz<sub>2</sub> (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)<sup>−</sup> and Ti(Bz)<sub>2</sub><sup>−</sup> 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

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a fixed frequency photon source and energy analyzing the resultant photodetached electrons. This technique is governed by the energy-conserving relationship  $h\nu = \text{EKE} + \text{EBE}$ , where  $h\nu$  is the photon energy, EKE is the measured electron kinetic energy, and EBE 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  $\sim 35$  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  $\text{Cu}^-$ .

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  $\sim 4$  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.

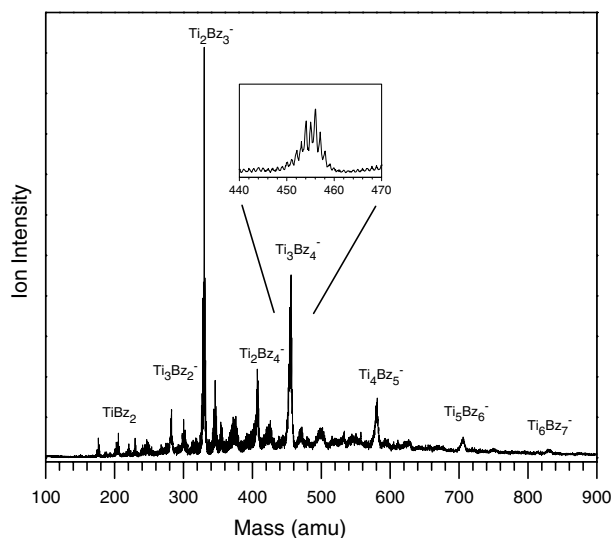


Fig. 1. A typical mass spectrum showing the  $\text{Ti}_n(\text{Bz})_m^-$  cluster anions studied in this work.

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  $\text{Ti}_3(\text{Bz})_4^-$ . 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  $\text{Ti}_n(\text{Bz})_{n+1}^-$  ( $n = 1-6$ ), although significant intensities of  $\text{Ti}_3(\text{Bz})_2^-$  and  $\text{Ti}_2(\text{Bz})_4^-$  are also seen routinely. Less often and under different source conditions, we also observed  $\text{Ti}_1(\text{Bz})_1^-$ . In the mass spectral/photoionization study by Kaya and coworkers [5], the most intense species observed was  $\text{Ti}_4(\text{Bz})_5^+$ .

The photoelectron spectrum of the  $\text{Ti}_1(\text{Bz})_1^-$  cluster anion is presented in Fig. 2, followed by the photoelectron spectra of  $\text{Ti}_n(\text{Bz})_{n+1}^-$  ( $n = 1-4$ ) cluster anions in Fig. 3 and the comparative photoelectron spectra of  $\text{Ti}(\text{Bz})_2^-$  and  $\text{Ti}_2(\text{Bz})_4^-$  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,  $\text{EA}_a$ , of the neutral cluster. Since the cluster anions have internal energy corresponding to a significant temperature, however, the EBE that designates the  $\text{EA}_a$  value is typically interpreted as lying

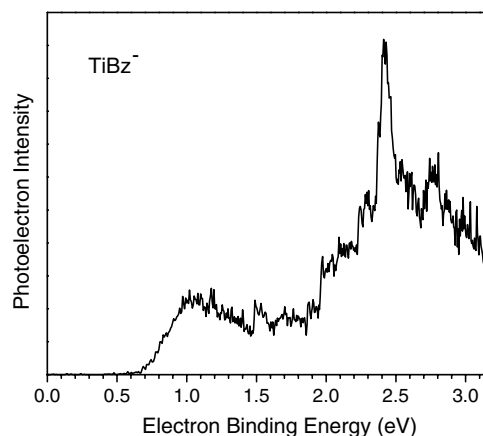


Fig. 2. The photoelectron spectrum of  $\text{Ti}_1\text{Bz}_1^-$  recorded with 355 nm photons.

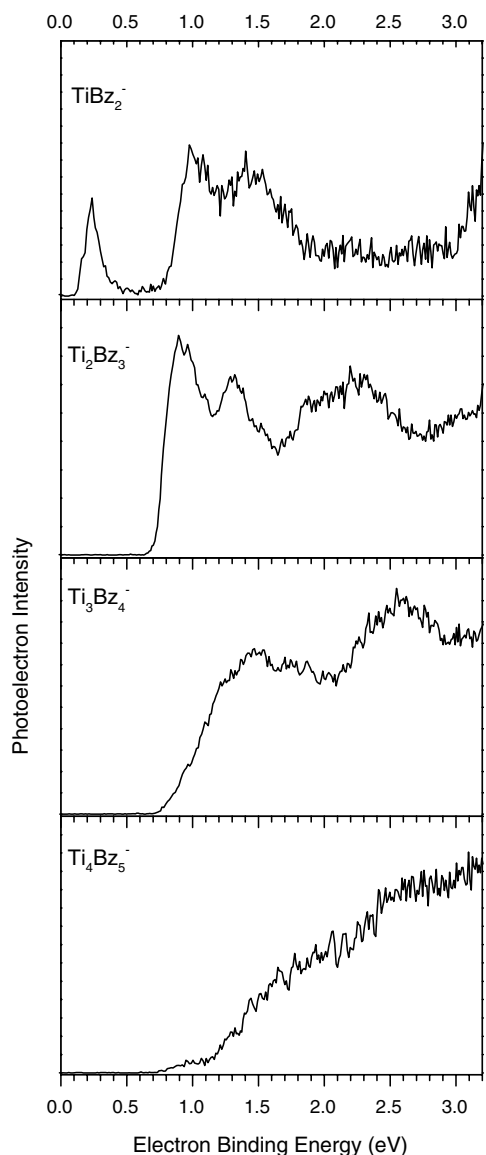


Fig. 3. The photoelectron spectra of the  $\text{Ti}_n(\text{Bz})_{n+1}^-$ ,  $n = 1-4$ , series, all recorded with 355 nm photons.

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,  $\text{EA}_a$  is approximately equal to VDE. Table 1 summarizes the VDE and  $\text{EA}_a$  values of the cluster systems studied here.

#### 4. Discussion

##### 4.1. $\text{Ti}_1(\text{Bz})_1^-$

Pandey et al. [16] calculated the adiabatic electron affinity for  $\text{Ti}_1(\text{Bz})_1$  to be 0.7 eV. The  $\text{EA}_a$  value for  $\text{Ti}_1(\text{Bz})_1$  derived from our measurements is

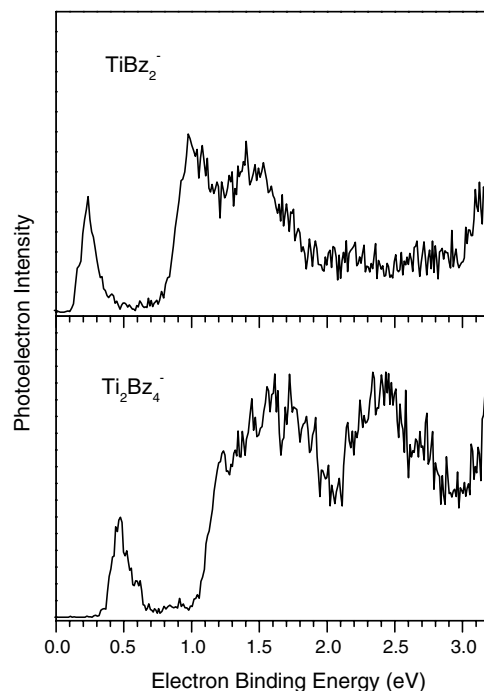


Fig. 4. The photoelectron spectra of  $\text{Ti}_1(\text{Bz})_2^-$  and  $\text{Ti}_2(\text{Bz})_4^-$ , both recorded with 355 nm photons.

Table 1

Vertical detachment energies, VDE, and adiabatic electron affinities,  $\text{EA}_a$ , of  $\text{Ti}_n(\text{Bz})_m$  clusters

$\text{Ti}_n(\text{Bz})_m$ cluster system	VDE (eV)	$\text{EA}_a$ (eV)
$\text{Ti}_1(\text{Bz})_1$	$1.05 \pm 0.050$	$0.85 \pm 0.150$
$\text{Ti}_1(\text{Bz})_2$	$0.23 \pm 0.050$	$0.18 \pm 0.060$
$\text{Ti}_2(\text{Bz})_3$	$0.90 \pm 0.075$	$0.80 \pm 0.1$
$\text{Ti}_3(\text{Bz})_4$	$1.4 \pm 0.2$	$1.0 \pm 0.2$
$\text{Ti}_4(\text{Bz})_5$	–	$1.5 \pm 0.5$
$\text{Ti}_2(\text{Bz})_4$	$0.47 \pm 0.050$	$0.40 \pm 0.070$

(All in eV).

$0.85 \pm 0.15$  eV (see Table 1 and Fig. 2), in accord with their theoretical prediction. This  $\text{EA}_a$  value is the transition energy between the electronic ground state of  $\text{Ti}_1(\text{Bz})_1^-$  and the electronic ground state of  $\text{Ti}_1(\text{Bz})_1$  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  $\text{Ti}_1(\text{Bz})_1$  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  $\text{Ti}_1(\text{Bz})_1$  is essentially  $4 \mu_B/\text{atom}$ . 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. $Ti_n(Bz)_{n+1}^-$

In examining the titanium–benzene cluster series,  $Ti_n(Bz)_{n+1}$ ,  $n = 1–4$ , 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  $Ti_n(Bz)_{n+1}^-$  series dominates the observed mass spectrum (see Fig. 1) is itself suggestive of alternating, multiple-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  $Ti(Bz)_2^-$ ,  $Ti_2(Bz)_3^-$ ,  $Ti_3(Bz)_4^-$  and  $Ti_4(Bz)_5^-$  are also consistent with this sandwich motif. In Fig. 3, one sees a gradual shift and evolution of  $Ti_n(Bz)_{n+1}^-$  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, eg., in going from  $Ti(Bz)_2^-$  to  $Ti_2(Bz)_3^-$ . (Table 1 shows the same gradual change as  $EA_a$  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  $Ti_n(Bz)_{n+1}^-$  spectra are compared with those of  $Ti_n^-$  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  $Ti_n(Bz)_{n+1}^-$  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  $Ti(Bz)_2$  to be sandwich structures with  $D_{6h}$  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  $Ti(Bz)_2$ , viz.,  $| \cdot |$ , 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 spectra of  $Ti_2(Bz)_3^-$  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  $Ti(Bz)_2^-$ 's sandwich structure into a double-layer sandwich structure for  $Ti_2(Bz)_3^-$ , viz.,  $| \cdot | \cdot |$ . While the photoelectron spectrum of  $Ti_3(Bz)_4^-$  is considerably broader than the spectrum of  $Ti_2(Bz)_3^-$ , we also interpret it as reflecting the sequential structural evolution from  $Ti(Bz)_2^-$  to  $Ti_2(Bz)_3^-$  to  $Ti_3(Bz)_4^-$ . We propose that  $Ti_3(Bz)_4^-$  is a triple-layer sandwich structure, viz.,  $| \cdot | \cdot | \cdot |$ . Due to its high density of states, there are no distinguishable features in the photoelectron spectrum of  $Ti_4(Bz)_5^-$ . Nevertheless, an evolved similarity with the spectrum of  $Ti_3(Bz)_4^-$  can be discerned, if one looks at the series as a whole. We speculate that the structure of  $Ti_4(Bz)_5^-$  is a quadruple-layer sandwich structure, viz.,  $| \cdot | \cdot | \cdot | \cdot |$ . All of the clusters in this series appear to have alternating, multiple-decker sandwich structures.

#### 4.3. $Ti_2(Bz)_4^-$ vs. $Ti(Bz)_2^-$

Fig. 4 compares the photoelectron spectra of  $Ti_2(Bz)_4^-$  and  $Ti(Bz)_2^-$ . The photoelectron spectrum of  $Ti_2(Bz)_4^-$  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  $Ti_2(Bz)_4^-$  and  $Ti(Bz)_2^-$  are quite similar, although the spectrum of  $Ti_2(Bz)_4^-$  has shifted to slightly higher EBE. We propose that  $Ti_2(Bz)_4^-$  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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