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The infrared spectrum of Al^+–benzene in the gas phase

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Abstract

The Al–benzene complex is produced by laser vaporization in a pulsed nozzle source. It is ionized with an ArF excimer laser (193 nm), and the Al^+(benzene) ions are stored in a quadrupole ion trap. Infrared excitation with a tunable free electron laser induces multiphoton photodissociation, and fragment ions are analyzed by a time-of-flight mass spectrometer. The infrared spectrum of Al^+(benzene) is measured with resonance-enhanced multiphoton photodissociation (IR-REMPD) spectroscopy. Bands in the 600–1800 cm^{-1} region correspond to benzene vibrations shifted by the metal bonding. The spectrum indicates that Al^+ binds in the symmetric $\eta^6\pi$ configuration on the benzene molecule.

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1. Introduction

Metal containing ion–molecule complexes that are produced, isolated and studied in the gas phase provide models for metal–ligand interactions and metal ion solvation [1]. Of these, metal–benzene ions are interesting because of their relevance for catalysis and biological processes [2], and for the fundamental importance that aromatic π-bonding has in organometallic chemistry [1,3,4]. Metal ion–benzene complexes may form sandwich structures or multiple-decker sandwich structures [5], and the electronic structure of such aggregates is not well understood. Metal–benzene complexes have also been synthesized in conventional chemistry (e.g., dibenzene–chromium [6]) and it is possible to compare gas phase unsaturated or charged species with complexes that have been isolated [3,4]. There are many mass spectrometric studies of the energetics of metal ion–benzene interactions and sandwich formation [5,7–11], but there are few studies of the spectroscopy of these species that provide specific insight into their structures and bonding [10–12]. Infrared spectroscopy has frequently been applied to study condensed phase metal–benzene complexes to investigate the strength of bonding via spectral shifts in the ligand-based vibrations [3,4]. However, such information has not been available for gas phase ion complexes. We have recently provided a brief communication on the first IR measurements of transition metal ion–benzene complexes [13].

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In the present Letter, we elaborate on this new methodology and provide the first data for Al^+(benzene) complexes.

Neutral metal–benzene complexes have been studied for many years in the condensed phase, as have some complexes with net charge that are produced and stabilized via counterions [3,4,6]. In this group, species such as dibenzene chromium have been investigated thoroughly with experiment and theory [3,4,6]. In gas phase studies, there are also many metal ion–benzene species that have been studied with mass spectroscopy, collision induced dissociation, ion mobility measurements and photodissociation [7–13]. Duncan and co-workers [10,11] have documented novel charge-transfer photodissociation processes that occur for many of these systems because of the close ionization energies between benzene and transition metals. Kaya and co-workers [5] reported the fascinating formation of multiple-decker sandwiches for a variety of transition metal–benzene complexes, especially those with vanadium. Theory has often examined the structures and energetics of these species [14–18]. Lisy and co-workers [12] have reported infrared spectroscopy on alkali cations bound to benzene in the C–H stretch region. However, until recently there were no vibrational spectroscopy measurements in other wavelength regions or for any other metal ion complexes with benzene. Our recent report on infrared resonance enhanced multiphoton dissociation (IR-REMPD) spectroscopy studies using a free electron laser documented IR spectroscopy on size-selected $V^+(\text{benzene})_{1,2}$ complexes [13]. These measurements were in the mid-IR, where benzene ring distortions and C–H bends occur that are sensitive to the nature of metal π-bonding.

Aluminum cation complexes with many small molecules have been studied with both theory and experiment [9,10,15,16,19–26]. Theory is particularly well suited for the aluminum cation because of its low number of electrons and its closed-shell electronic structure. Aluminum ion complexes exhibit fascinating chemistry, especially regarding charge separation and solvation dynamics [21,25]. Electronic spectroscopy is problematic for Al^+ complexes because the first excited state of Al^+ lies at a very high energy, but there has been some recent success with electronic photodissociation spectroscopy measurements [23,24]. Aluminum and its complexes have low ionization potentials, and therefore photoionization can be used to produce cation complexes in their ground states [20,25]. High resolution photoelectron spectroscopy has been employed for vibrational information in the cation ground states [26], but the Franck–Condon activity is in the Al^+–ligand stretching coordinates and not in the ligand-based modes. Al^+–benzene itself has been studied with mass-selected photodissociation [10], and with radiative association kinetics to derive bonding energetics [9]. Its structure and bonding have been examined with various computational methods [15], but there are no previous calculations reporting vibrational frequencies. IR spectroscopy would be valuable to complement these various studies. Until recently, IR spectroscopy was not generally possible on metal ion complexes because of low ion densities and the unavailability of broadly tunable IR laser sources. However, the IR-REMPD method overcomes these problems [13]. In the present work, this method is applied to the Al^+(benzene) complex, and the vibrational spectrum measured is compared to the results of theoretical calculations.

2. Experimental

Aluminum–benzene complexes are produced by laser vaporization of a solid metal rod in a pulsed nozzle (Jordan valve) source using an argon expansion seeded with benzene vapor. Neutral complexes in the molecular beam pass through the center of an ion trap mass spectrometer (Jordan), where they are ionized with an ArF excimer laser (Neweks, PSX-100) (193 nm; 6.42 eV; 4 mJ/pulse). The ionization potential of aluminum (5.99 eV) is lower than the ArF photon energy and aluminum–benzene apparently also has a low ionization potential because efficient ionization occurs at this wavelength. The cation complexes are trapped for several milliseconds, and isolated by mass with the RF potentials (1 MHz; up to ~1000 V p–p) of the trap. In the present configuration, no collision gas is used to stabilize the trajectories of trapped ions.

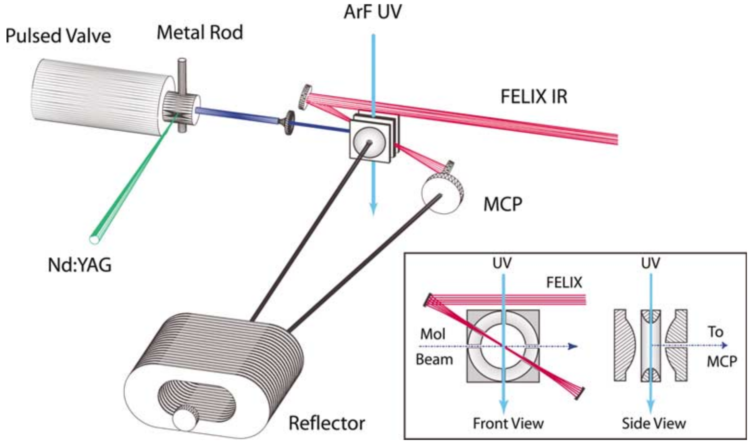

Fig. 1. The configuration for this experiment showing the pulsed nozzle laser vaporization cluster source, the ion trap mass spectrometer and the ArF ionization and FELIX photodissociation lasers.

Because of this, mass selection of specific ions is not possible, but rather ions below a certain threshold can be rejected from the trap by adjustment of the RF potential. In the present experiment, ions below the mass of Al^+(benzene) are eliminated in this way, allowing the Al^+ photofragment to be detected on a zero background. Tunable infrared excitation is accomplished with the free electron laser for infrared experiments (FELIX) [27], which produces intense pulses with energies of 40–60 mJ throughout the spectral region of this experiment (600–1800 cm^{-1}). After excitation with FELIX, the contents of the ion trap are extracted into a reflectron time-of-flight spectrometer for mass analysis. Infrared absorption leads to resonance enhanced multiphoton dissociation (IR-REMPD), which is evident from the appearance of Al^+ fragment ions following IR excitation. The Al^+ yield is recorded as a function of the wavelength to obtain an infrared spectrum of the parent ion. A schematic diagram of this experiment is shown in Fig. 1. The general methodology for these experiments has been described previously for studies of polycyclic aromatic hydrocarbon (PAH) cations [28], for $Ti_8C_{12}^+$ [29] and for $V^+(benzene)_{1,2}$ [13].

Theoretical calculations are performed with the GAUSSIAN 98 suite of programs [30] using density functional theory (DFT) and the B3LYP functional. The aug-cc-pvtz basis (464 functions) is employed throughout. The harmonic vibrational frequencies calculated are presented without any corrections or scaling. Calculations are carried out on the free benzene molecule at the same level of theory to verify the effect of this approximation on the vibrational frequencies of the complex.

3. Results and discussion

Fig. 2 shows the mass spectra observed for aluminum benzene complexes with and without excitation by FELIX. The only complex ion produced by the source and detected with ArF ionization under these conditions is Al^+(benzene). Larger complexes can be produced under other conditions, as we have reported elsewhere [10,11]. As shown, the only fragment from IR excitation of Al^+(benzene) is the Al^+ ion, consistent with the previous observation of the UV photodissociation of this ion [10]. The dissociation energy of $Al^+(C_6H_6)$ has been measured with radiative association kinetics to be 35.2 kcal/mol ($\sim$12,300 cm^{-1}) [9]. It is therefore clear that the IR photodissociation seen here must be a multiphoton process. However, multiphoton processes involving up to 600 photons have been measured previously with FELIX for the photoionization of fullerenes [31,32] and metal carbide [33] clusters.

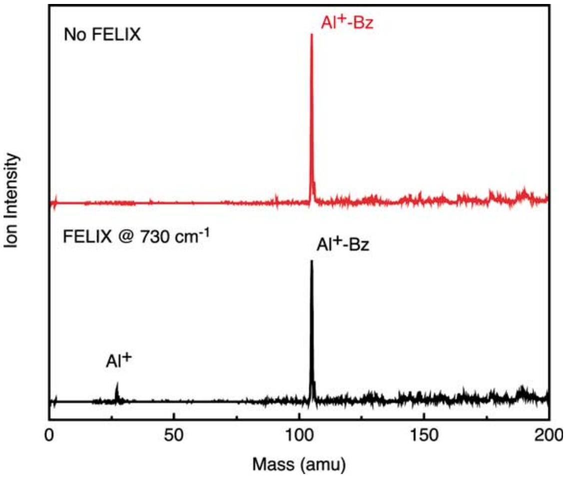

Fig. 2. The mass spectrum of Al^+(benzene) complexes produced by ArF laser ionization of neutral complexes, and the photodissociation to produce Al^+ fragment ions via IR-REMPD.

When the IR laser used for photodissociation is scanned, fragmentation only occurs at specific wavelengths, and this is attributed to resonance enhancement of the multiphoton absorption and subsequent dissociation when the laser is tuned to vibrational resonances. The IR-REMPD spectra obtained for $Al^+(C_6H_6)$ by measuring the Al^+ fragment ion yield versus wavelength is shown in Fig. 3, and the IR band positions are shown in Table 1. Strong bands are measured near 700 and 1500 cm^{-1} and a moderate intensity band occurs near 1000 cm^{-1}. The linewidths in these spectra are somewhat broad, i.e., about 60–70 cm^{-1} FWHM. These are believed to arise from a combination of effects including the thermal populations produced by ionization and the dynamics of multiphoton excitation [31,32]. Similar broad bands were obtained in previous work on PAH cations [28], $Ti_8C_{12}^+$ [29] and $V^+(benzene)_{1,2}$ complexes [13]. We therefore assign an uncertainty to the exact line positions of ± 10 cm^{-1}. Although these bandwidths are broad by gas phase spectroscopy standards, they are comparable to those measured for condensed phase IR spectroscopy. By comparison with previous IR spectra of metal–benzene complexes in the condensed phase (e.g., dibenzene chromium) [3,4], the vibrational bands here can immediately be recognized as those associated with the benzene molecule perturbed by the metal bonding interactions. Table 1 compares these band positions to those of free benzene [34], the known dibenzene chromium complex [3,4], the recently measured V^+(benzene) complex [13], and to our predictions from theory. Fig. 3 shows the corresponding free benzene mode positions as dashed vertical lines.

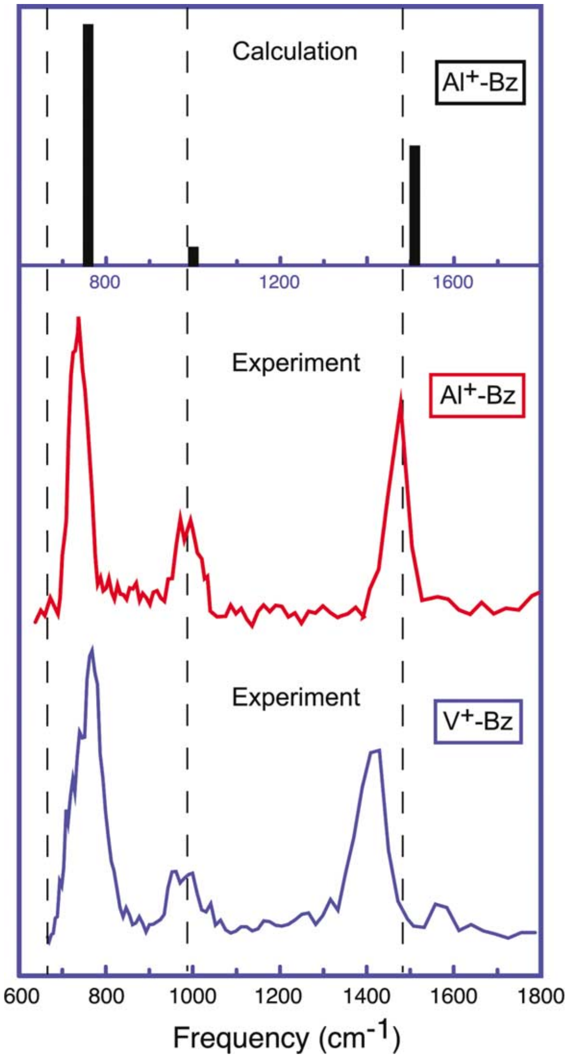

Fig. 3. The IR-REMPD spectrum of Al^+–benzene measured in the Al^+ fragment channel and the comparison to theory. The dashed vertical lines indicate the positions of vibrations in the free benzene molecule.

The band seen at 730 cm^{-1} can be assigned to the ν_{11} mode of free benzene (out-of-plane H

Table 1
Vibrations measured for Al^+(benzene) and the comparison to theory

	19 i.p. C ring dist.	18 i.p. C–H bend	1 sym. C stretch^a	11 o.o.p. H bend	Al^+-ring stretch
C_6H_6 (gas phase) [34]	1486	1038	992	673	–
C_6H_6 (theory, this work)	1515	1060		693	
$Cr(C_6H_6)_2^4$	1426	999	971	794	
$Al^+(C_6H_6)$ (theory)	1509 (63)	1054 (0.8)	1001 (6.0)	760 (129)	205 (85)
$Al^+(C_6H_6)$ (this work)	1481		990	730	
$V^+(C_6H_6)$ (exp.) [13]	1425		980	769	

IR intensities are given in parentheses. The mode numbers refer to isolated benzene vibrations in the Wilson numbering scheme.
^{a} IR inactive in C_6H_6.

bend), and this band is significantly blue-shifted from the corresponding frequency of free benzene (673 cm^{-1}). The band at 990 cm^{-1} could correspond to either the ν_{18} mode (in-plane C–H bend; 1038 cm^{-1} in C_6H_6) or to the ν_1 mode (symmetric C stretch; 992 cm^{-1} in C_6H_6). However, although ν_1 is not IR-active in free benzene, it becomes active in the complex and is calculated to have a much greater IR intensity than the ν_{18} mode (see below). The band observed is therefore assigned to the ν_1 mode, which is then red-shifted by only 2 cm^{-1} with respect to free benzene. The other strong band at 1481 corresponds to the ν_{19} mode (in-plane C ring distortion; 1486 cm^{-1} in C_6H_6) which is also only slightly red-shifted from the free benzene mode.

These same vibrational modes are observed in the spectra of many known transition metal–benzene complexes in the condensed phase, and their shifts relative to the free benzene modes have been discussed extensively [3,4]. In the so-called Dewar–Chatt–Duncanson model of π-bonding, the transition metal withdraws electron density from the benzene π orbitals, and back-donates metal d electron density into the benzene π* orbitals. Both effects weaken the bonding of the ring system and make the ring-based vibrations less rigid. The ν_1 and ν_{19} vibrations in transition metal–benzene complexes are then usually shifted to lower frequencies compared to the free molecule. In their theoretical study of these systems, Chaquin and co-workers [17] point to the $\nu_{19}(e_1)$ vibration in particular as the key indicator of the benzene-to-metal charge transfer. By contrast to this, the out-of-plane C–H bend (ν_{11}) in transition metal complexes shifts to *higher* frequency because of the added metal repulsion near the turning points of this vibration. Table 1 shows the vibrations known for $Cr(benzene)_2$ [4,5] and those measured recently for the corresponding V^+(benzene) complexes using this same IR-REMPD method [13], which both illustrate this classic behavior. Fig. 3 also shows the V^+(benzene) vibrational spectrum where these shifts are readily apparent. The red-shift for the ν_{19} mode in V^+(benzene) is about 90 cm^{-1}. As shown here, however, the Al^+(benzene) complex provides an interesting contrast to this familiar behavior in transition metal systems. The ν_{11} vibration is indeed shifted to the blue just like the transition metal systems. This is because the source of this shift (additional repulsion near the bending mode turning point) is more physical than chemical in origin. On the other hand, the ν_1 and ν_{19} modes, which are indicative of the charge-transfer nature of the chemical bonding, are hardly shifted at all from the free benzene modes. This is understandable because the bonding in the aluminum complex should have virtually no covalent component, but should instead be essentially electrostatic (charge-induced dipole) in nature. There are no empty d orbitals at low energy to accept charge nor filled d orbitals to back-donate charge. The relative M^+–(benzene) bond energies (e.g., 54.2 kcal/mol for V^+ [7] versus 35.2 kcal/mol for Al^+ [9]) are consistent with the picture of mostly electrostatic bonding for aluminum and more covalent character for the transition metal. The bond energy trends between transition metal and non-transition metal complexes have been known and appreciated for some time. However, this is the first time that these differences can be viewed from the standpoint of the vibrational spectrum.

Our theoretical calculations find a singlet ground state, as expected, and the structure of the complex is the symmetric C_{6v} with the metal ion located on the sixfold axis 2.413Å above the plane of the ring. C–C and C–H bond distances are 1.398 and 1.081 Å, respectively. The Al^+–benzene binding energy is computed to be $D_0 = 30.2$ kcal/mol (1.31 eV), in good agreement with experiments [9]. This value is somewhat lower than the previously computed value of 35.6 kcal/mol reported by Stöckigt [15]. The infrared bands computed for the free benzene molecule and for this complex are shown in Table 1. The relative intensities are indicated in the table in parentheses and for the stronger bands by the bars in Fig. 3. We have only investigated one functional and basis set believed from previous experience to be appropriate for this system. Extensive investigations at other levels of theory have been reported by Stöckigt [15] as they affect the binding energy and structural parameters. The free benzene vibrations are reasonably well described by theory, but are slightly higher than the experimental values. This is expected for harmonic frequencies calculated with DFT. We have not shifted or scaled the vibrations calculated for the complex.

It is pleasing to note the good agreement between these measurements and the predictions of theory, as indicated in Table 1 and in Fig. 3. The calculations reproduce both the band positions and the relative band intensities observed for the most prominent features. As noted above for the free benzene at this same level of theory, the calculated vibrations are systematically slightly higher than the experimental ones. Because of the good agreement, we can conclude that the Al^+(benzene) complex does indeed have the symmetric bonding configuration predicted by theory with the metal ion on the sixfold axis. The general structure of the complex and the nature of the bonding as exemplified by the vibrational structure are consistently described here. Although the C_{6v} structure has been the consensus of previous theory, this is the first spectroscopic confirmation of this structure. It is understandable that these calculations would be reasonably successful for Al^+(benzene) complexes because of the simple electronic structure on the metal. All levels of theory agree on the general nature of the bonding (electrostatic) and all are in reasonable agreement on the binding energies [15]. The vibrations have not been calculated before, but it is pleasing to see the close agreement between theory and experiment. As we have recently described, theory on similar benzene complexes with transition metals is much more problematic, especially regarding issues of electronic spin states [13]. On the other hand, it is actually somewhat surprising that the band *intensities* calculated here reproduce those measured with IR-REMPD. The calculated intensities are those for one-photon *absorption*, while the IR-REMPD represents a much more complex process. However, if we assume that intramolecular vibrational relaxation (IVR) is rapid in these complexes, the initial absorption event could be the rate limiting step leading to dissociation, and thus it is perhaps understandable that absorption and IR-REMPD intensities could match well.

Kaya and co-workers [35] have recently found evidence for isomeric structures of *neutral* Al–benzene complexes in which the metal is located in either the η^6 position above the benzene ring or localized above a C–C bond. However, it is known that the structures of corresponding neutral and ionized aluminum complexes may be quite different [26]. The bonding for the closed-shell Al^+(benzene) is expected to be largely electrostatic and dominated by the charge-induced dipole and charge-quadrupole interactions. Isomeric structures are therefore not expected and there is no evidence for them in either the experiment or the theory.

This work demonstrates the utility for gas phase vibrational spectroscopy to probe the details of bonding interactions in metal–ion benzene complexes without the complications of solvent interactions. Significant qualitative differences are seen in the vibrational shifts of the Al^+(benzene) complex measured here compared to previously studied transition metal–benzene complexes. Consistent with the predictions of theory, the ν_{19} vibration seems to be a sensitive indicator of the charge transfer. In transition metal complexes, this vibration shifts strongly to the red, but in Al^+(benzene) there is essentially no shift. A crucial aspect of the experiment is the tunable free electron laser that provides high power IR light in the mid-IR where benzene ring based vibrations occur. These experiments should be general for a variety of other main group and transition metal ion complexes with benzene or other related ligands that exhibit π-bonding.

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