Photoionization studies of benzene-argon complexes with synchrotron VUV radiation

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INTRODUCTION

Complexes of benzene and argon are prototypes of rare gas/aromatic molecule systems. Consequently, they have been studied extensively, both experimentally and theoretically.

Much effort has been directed at a detailed understanding of the ground state structure and potential energy surface (PES). The neutral 1:1 ground-state (Sa) complex, \(C_6H_6–Ar\), has \(C_{6v}\) symmetry with the Ar 3.58 Å from the center of the benzene ring,\(^a\) and the dissociation energy, \(D_0\), is \(314 \pm 7 \text{ cm}^{-1} (0.90 \pm 0.02 \text{ kcal mol}^{-1})\).\(^b\) Other conformations with some stabilization have also been calculated,\(^c\) but the stabilization energies are not as great as that for \(C_{6v}\) symmetry. The ionization energy of the complex is 74 387.253 ± 0.02 cm\(^{-1}\) (9.222 918 ± 0.000 002 5 eV).\(^d\)\(^e\) Theoretical results are in good agreement with the experimental observations and their interpretation.\(^f\)\(^g\)\(^h\)\(^i\) Therefore, the intermolecular PES of \(C_6H_6–Ar\) is well understood.

The dissociation energy of the 1:1 ionic complex, \((C_6H_6)\(^+\)–Ar\(^–\))\(^a\), has been measured,\(^i\) \(D[(C_6H_6)\(^+\)–Ar\(^–\)] = 486 ± 5 \text{ cm}^{-1} (1.39 ± 0.01 \text{ kcal mol}^{-1})\).

For the 1:2 neutral complexes \(C_6H_6–Ar_2\), and \(C_6D_6–Ar_2\), two isomers (conformers) have been identified, (1|1) and (2|0).\(^j\)\(^k\)\(^l\)\(^m\) The (1|1) \(Ar–C_6H_6–Ar\) isomer has a symmetric top \(D_{4h}\) ground state\(^n\)\(^o\)\(^p\) with benzene-Ar distances both 3.58 Å, specifically for the (1|1) \(Ar–C_6H_6–Ar\).\(^q\) Less information has been reported for the (2|0) complexes, although calculations show the (1|1) complex to be the more stable while molecular dynamics find that the relative populations of the (2|0) to (1|1) species are 64:36 between 27 and 37 K, temperatures typical of molecular beam expansions.\(^s\) The higher population for the (2|0) isomer is attributed to an entropy effect; that is, there are a larger number of equivalent configurations for the (2|0) case than those for (1|1).

Experimental studies of \(C_6H_6–Ar_m\) (and \(C_6D_6–Ar_m\), where \(m > 2\), are sparse. Relaxation rates have been determined\(^t\) as intramolecular vibrational redistributions,\(^u\)\(^v\)\(^w\) and isomers (conformers) have been identified,\(^x\) especially for (3|0) \(C_6H_6–Ar_3\).\(^y\) Theoretical studies have been reported for \(C_6H_6–Ar_m\), \(m = 3–5\) and for \(m = 2–8\),\(^z\)\(^{14}\) using a constant-energy molecular dynamics simulation with an \textit{ab initio} intermolecular potential for the \(C_6H_6–Ar\) interaction; thus, their structures and relative populations of the various isomers were determined.

All of this work deals with ground state structures. However, significant insight into higher energy processes of charge and energy transfer can be obtained from resonances in photoionization...
The product ions were extracted, mass selected, and measured in the photon beam in the ionizer of a quadrupole mass spectrometer and sometimes between runs on the same fill, to adjust for minor threshold of argon was carried out for each fill of the storage ring, as described in Ref. 33. Measurement of the apparent ionization was inserted to eliminate second and higher order radiation. Otherwise, corrections for second and third order radiation were made.

Below 11.3 eV (1100 Å), a 0.2 cm thick lithium fluoride window was used to emphasize small clusters. The nozzle temperature was maintained at 15°C.

The inventory of principal ions at 800 Å (below the energy for ionizing Ar but above that for ionizing Ar2) is shown in Fig. 1. No attempt to optimize further the production of benzene-argon mixed clusters was made.

**RESULTS AND DISCUSSION**

**Dissociation energies of C6H6–Ar and C6H6–Ar**

The dissociation energy, C6H6–Ar + h ν → C6H6 + Ar + e, was measured using the method described in Ref. 35. Figure 2 shows the onset of C6H6 from C6H6–Ar at 9.279 ± 0.004 eV by dissociative ionization of the complex.

A second experiment gave essentially the same result, 9.286 eV. Since IP(C6H6) = 9.244 eV, the averaged dissociation energy of the neutral complex is 0.08 ± 0.07 kcal mol⁻¹ (i.e., 0.039 ± 0.003 eV). Using the ionization potential of C6H6–Ar of 9.2229 eV, the C6H6–Ar⁺ dissociation energy is 1.37 ± 0.08 kcal mol⁻¹ (i.e., 0.059 ± 0.035 eV). For comparison, Sampson and Lawrance measured these values to be 0.90 ± 0.02 and 1.39 ± 0.01 kcal mol⁻¹ using velocity map imaging, a much more precise method. This result
estabishes that the apparatus used in these experiments functions reliably and reproducibly.

Penning ionization of Rydberg states

Ionization of every complex of benzene and argon shows two peaks between 11.5 and 12 eV that correspond to argon states in which the five 3p electrons couple to $\frac{1}{2}$ and $\frac{3}{2}$ and these couple to the 4s electron to form $j = 1$. In the present experiment, these states are observed in the ions $C_6H_6^+$, $C_6H_6Ar^+$, $C_6H_6Ar_2^+$, $C_6H_6Ar_3^+$, $(C_6H_6_2)^+$, and $(C_6H_6_2)Ar^+$. Note that $C_6H_6^+$ and $(C_6H_6_2)^+$ must come from clusters with at least one argon atom in order to exhibit IPI.

The states corresponding to $j = 0$ and $j = 2$ are weaker, and the apparatus is not sensitive enough to show them.

The peaks are fitted to the nonrelativistic Breit-Wigner line shape expression

$$\sigma(\epsilon, C, \Gamma) = k((\epsilon - C)^2 + (\Gamma/2)^2)^{-1},$$

where $k$ is a constant, $\epsilon$ is photon energy, $C$ is the center energy, and $\Gamma$ is the width of the peak at half-maximum. This is a Lorentzian line shape function in a convenient form for extracting the line shape parameters $C$ and $\Gamma$. The data were fitted using a least squares procedure to obtain $C$ and $\Gamma$ for the observed ions as a function of nozzle pressure. The results are collected in Table I.

Consider first the $C_6H_6^+$ ion, m/e 78. This ion comes from direct photoionization of $C_6H_6$ and from dissociative photoionization of $C_6H_6$–Ar, $C_6H_6$–Ar + hv $\rightarrow C_6H_6^+$ + Ar + e$. At the lowest nozzle pressures, 251–350 Torr, only two narrow peaks are observed slightly red-shifted (~0.06 eV) from the positions of the argon atom transitions [see Table I(a)]. These are evidence of IPI.

As the nozzle pressure is increased, two new peaks appear in the spectrum. At a pressure of 400 Torr signs of the largest of these peaks are present (see Fig. 3). These peaks are broad and are blue-shifted from the atomic argon transitions by 0.03–0.06 eV. They grow quickly with increasing nozzle pressure such that the narrow and broad peaks are of comparable magnitude at 450 Torr, as shown

![Graph showing net counts of C₆H₆Ar](image)

**FIG. 2.** Threshold region of C₆H₆⁺ ions from the dissociative ionization of C₆H₆–Ar, observed as the difference of intensity between C₆H₆⁺ ions produced at 500 Torr of nozzle pressure and C₆H₆⁺ ions produced at 250 Torr.

### Table I. Line shape parameters $C$, line center in eV, and $\Gamma$, full width at half-maximum in eV, for the ions studied in this experiment as a function of nozzle pressure, $P$, in Torr. Subscripts $n$ and $w$ refer to narrow and wide peaks, while hi and lo indicate the higher and lower energy Ar-atom Rydberg transitions, respectively.

| $P$ (Torr) | $C_{whi}$ | $\Gamma_{whi}$ | $C_{nhi}$ | $\Gamma_{nhi}$ |
|------------|-----------|----------------|-----------|----------------|
| (a) $C_6H_6^+$ (narrow) | | | | |
| 251 | 11.76 | 0.026 | 11.56 | |
| 300 | 11.76 | 0.025 | 11.55 | |
| 350 | 11.76 | 0.024 | 11.57 | |
| 400 | 11.76 | 0.022 | 11.56 | 0.057 |
| 450 | 11.77 | 0.027 | 11.57 | 0.063 |
| 500 | 11.79 | 0.026 | 11.60 | 0.082 |
| 500 | 11.78 | 0.022 | 11.59 | 0.044 |
| 700 | 11.77 | 0.020 | | |

| (b) $C_6H_6^+$ (wide) | | | | |
| 400 | 11.89 | 0.054 | | |
| 450 | 11.89 | 0.109 | 11.65 | 0.038 |
| 500 | 11.91 | 0.215 | 11.69 | 0.050 |
| 600 | 11.90 | 0.214 | 11.67 | 0.060 |
| 700 | 11.89 | 0.220 | 11.66 | 0.106 |
| 800 | 11.89 | 0.227 | 11.66 | 0.103 |
| 900 | 11.90 | 0.221 | 11.67 | 0.112 |
| 988 | 11.91 | 0.209 | 11.69 | 0.109 |

| (c) $(C_6H_6)_2^+$ (wide) | | | | |
| 500 | 11.86 | 0.337 | 11.65 | 0.121 |
| 998 | 11.94 | 0.234 | 11.71 | 0.100 |

| (d) $C_6H_6Ar^+$ (narrow) | | | | |
| 200 | 11.78 | 0.028 | 11.57 | |
| 300 | 11.77 | 0.032 | 11.57 | |
| 400 | 11.77 | 0.032 | 11.57 | |
| 500 | 11.76 | 0.030 | 11.55 | 0.035 |
| 600 | 11.76 | 0.030 | 11.56 | 0.042 |
| 700 | 11.76 | 0.029 | 11.56 | 0.037 |
| 800 | 11.76 | 0.027 | 11.56 | |
| 900 | 11.77 | 0.034 | 11.58 | |
| 998 | 11.78 | 0.027 | 11.58 | |

| (e) $C_6H_6Ar^+$ (wide) | | | | |
| 500 | 11.92 | 0.083 | 11.66 | 0.072 |
| 600 | 11.89 | 0.197 | 11.65 | 0.071 |
| 700 | 11.89 | 0.203 | 11.65 | 0.080 |
| 800 | 11.89 | 0.226 | 11.65 | 0.123 |
| 900 | 11.92 | 0.220 | 11.67 | 0.099 |
| 998 | 11.92 | 0.237 | 11.68 | 0.133 |
TABLE I (Continued.)

| P (Torr) | C\_nhi | \( \Gamma_{nhi} \) | C\_nlo | \( \Gamma_{nlo} \) |
|----------|--------|----------------|--------|----------------|
| (f) \( {C_6H_6Ar}^+ \) (narrow) | | | | |
| 300 | 11.78 | 0.032 | 11.58 | 0.043 |
| 500 | 11.78 | 0.028 | 11.58 | 0.034 |
| 700 | 11.76 | 0.025 | 11.56 | 0.041 |
| 900 | 11.76 | 0.030 | | |
| P C\_whi | \( \Gamma_{whi} \) | C\_wlo | \( \Gamma_{wlo} \) |
| (g) \( {C_6H_6Ar}^+ \) (wide) | | | | |
| 700 | 11.88 | 0.225 | 11.66 | 0.087 |
| 900 | 11.90 | 0.224 | 11.66 | 0.131 |
| 998 | 11.92 | 0.278 | 11.69 | 0.126 |
| P C\_whi | \( \Gamma_{whi} \) | C\_wlo | \( \Gamma_{wlo} \) |
| (h) \( {C_6H_6Ar}^+ \) (wide) | | | | |
| 998 | 11.91 | 0.272 | 11.68 | 0.176 |
| 1000 | 11.91 | 0.233 | 11.71 | 0.351 |
| 1200 | 11.92 | 0.207 | 11.68 | 0.181 |
| P C\_whi | \( \Gamma_{whi} \) | C\_wlo | \( \Gamma_{wlo} \) |
| (i) \((C_6H_6)Ar^+\) (wide) | | | | |
| 998 | 11.92 | 0.196 | 11.68 | 0.185 |
| 1200 | 11.93 | 0.204 | 11.69 | 0.187 |

FIG. 4. At a nozzle pressure of 700 Torr, the narrow peaks (red) of \( \text{C}_6\text{H}_6^+ \) are comparable in intensity to the blue-shifted (blue) peaks.

Two different environments. The characteristics of these two sets of peaks is as follows:

1. The presence of two very different sets of IPI peaks, one of which is largely independent of nozzle pressure and the other which responds to increased nozzle pressure by rapidly becoming the dominant spectral feature. The low-pressure peaks are narrow, while the higher pressure peaks are broad. The widths of these peaks remain very similar to one another over the range of pressures and species examined. Neither the line positions nor their widths vary significantly with either nozzle pressure or cluster size.

2. The energies of the narrow peaks are red-shifted by about 0.06 eV (1.4 kcal mol\(^{-1}\)) from the corresponding Ar atomic levels at 11.8282 and 11.6237 eV.\(^{38,39}\) The energies of the wide peaks in Fig. 4. At a nozzle pressure of 700 Torr, the red-shifted narrow peaks (red) are difficult to discern (see Fig. 5). The line shape parameters for the wide peaks are found in Table I(b).

The existence of two distinctly different sets of IPI peaks strongly suggests that argon giving rise to these peaks is found in two different environments. The characteristics of these two sets of peaks is as follows:

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peaks are blue-shifted by about 0.07 eV (1.6 kcal mol\(^{-1}\)) and 0.05 eV (1.2 kcal mol\(^{-1}\)).

3. The peak widths are consistent with rapid energy transfer from an excited Ar atom to benzene above the ionization threshold accompanied by ionization of the benzene partner resulting in narrow peaks and a more complex process yielding broader peaks.

4. The broader peaks grow in proportion as the nozzle pressure increases, a situation that favors the formation of larger, more complex clusters, and in the presence of a great surplus of Ar, a tendency to form \(\text{C}_6\text{H}_6\text{Ar}_n\), \(n > 1\).

These observations are consistent with the interpretation of narrow and wide peaks offered by Kamke et al.,\(^\text{31}\) that narrow peaks arise from an Ar atom located at the surface of the benzene molecule in the cluster, whereas the broad peaks come from an Ar atom embedded in a group of two or more Ar atoms.

The broadening of the blue-shifted peaks may be the result of a quasistatic form of pressure broadening arising from van der Waals interactions among the cluster constituents and their orientation with respect to one another. The result is a collection of superimposed narrow lines with slightly different energies giving a spectrum that appears to be continuous. In principle, a careful analysis of the wings of the broad peaks could distinguish the actual line shapes, and therefore, the source of the broadening but scatter in the data does not allow this analysis.

Turning now to the \((\text{C}_6\text{H}_6)_2\)\(^+\) case, this ion must originate in a cluster containing one or more Ar atoms because the wavelength scan through the IPI region shows two prominent Penning ionization peaks [see Fig. 6 and Table I(c)]. These are the broad, blue-shifted peaks and they do not appear until the nozzle pressure is relatively high, despite the continual growth in the yield of \((\text{C}_6\text{H}_6)_2\)\(^+\) with increasing pressure (see Fig. 1). Furthermore, these spectra are distinguished by the complete absence of any indication of the pair of narrow peaks so characteristic of all other spectra.

Using a slight modification of the Kamke et al. interpretation,\(^\text{31}\) the presence of broad peaks only strongly suggests that the Ar atom in the parent \((\text{C}_6\text{H}_6)_2\)\(^+\)–Ar cluster is sandwiched between the benzene molecules, \(\text{C}_6\text{H}_6\)–Ar–\(\text{C}_6\text{H}_6\) making it subject to more intermolecular interactions and giving rise to the blue shift. The broad line width again may be due to ionization of multiple configurations of the neutral cluster, which differ energetically from one another by a small amount. Nevertheless, it is recognized that the observed \((\text{C}_6\text{H}_6)_2\)\(^+\) ions have at least two sources: \((\text{C}_6\text{H}_6)_2\) and \((\text{C}_6\text{H}_6)_2\)–Ar by dissociative ionization \((\text{C}_6\text{H}_6)_2\)–Ar + h\(\nu\) → \((\text{C}_6\text{H}_6)_2\)\(^+\) + e\(^-\) + Ar. The \((\text{C}_6\text{H}_6)_2\)\(^+\) ions from dissociation are much more intense than the \((\text{C}_6\text{H}_6)_2\)–Ar\(^-\) ions from direct ionization of a \((\text{C}_6\text{H}_6)_2\)–Ar cluster.

The ion \(\text{C}_6\text{H}_6\text{Ar}^+\) also displays narrow peaks [see Table I(d)], but the narrow peaks are clearly discernable up to a pressure of at least 998 Torr. They are found at essentially the same energies as in the \(\text{C}_6\text{H}_6\) ions. This is to be expected from the ionization of \(\text{C}_6\text{H}_6\text{Ar}\), but a comparison with the behavior of \(\text{C}_6\text{H}_6^+\) shows that \(\text{C}_6\text{H}_6\text{Ar}^+\) ions also arise from \(\text{C}_6\text{H}_6\text{Ar}_2\) by dissociative ionization. Any change in peak energy is too small to detect.

Note that the width for the peak of higher energy is slightly broader. This could be a true widening or it could be an apparent widening because the observed “peak” is three peaks of slightly different energies: (1) ionization of \(\text{C}_6\text{H}_6\text{Ar}\), (2) the dissociative ionization of the \((1|1)\) isomer of \(\text{C}_6\text{H}_6\text{Ar}_2\), and (3) the dissociative ionization of the \((2|0)\) form of \(\text{C}_6\text{H}_6\text{Ar}_2\). The number of argon atoms does not change the peak energies enough to detect.

The widths of the peaks of lower energy are too poorly determined to permit a similar discussion.

As observed for \(\text{C}_6\text{H}_6^+\), broader peaks develop for \(\text{C}_6\text{H}_6\text{Ar}^+\) with increasing nozzle pressure [see Table I(e)]. The similarities of the energies and widths of the peaks to those seen for \(\text{C}_6\text{H}_6^+\) are striking. Here, the amounts of the narrow and wide peaks are comparable at a nozzle pressure of about 700 Torr (Fig. 7).

Since the amounts of the narrow and wide peaks are comparable at 450 Torr for \(\text{C}_6\text{H}_6\)\(^+\), it appears that the dissociative ionization of \((\text{C}_6\text{H}_6)_2\)Ar leads mostly to \(\text{C}_6\text{H}_6\)\(^+\) and much less to \(\text{C}_6\text{H}_6\text{Ar}^+\). Thus, assuming most of the \(\text{C}_6\text{H}_6\text{Ar}^+\) comes from dissociative ionization of \(\text{C}_6\text{H}_6\text{Ar}_2\) and \((\text{C}_6\text{H}_6)_2\)Ar, it is estimated that \(\text{C}_6\text{H}_6\text{Ar}_2\)

![FIG. 6. Peaks at 11.94 and 11.71 eV, showing that Ar is bound to the cluster from which the \((\text{C}_6\text{H}_6)_2\)\(^+\) ion originates, most likely \((\text{C}_6\text{H}_6)_2\)Ar.](image1)

![FIG. 7. At a nozzle pressure of 700 Torr, the red-shifted and blue-shifted peaks of the \(\text{C}_6\text{H}_6\text{Ar}^+\) ions are comparable in intensity.](image2)
and (C₆H₆)₂Ar₂ make similar contributions to the composition of the molecular beam at 700 Torr.

The nozzle pressure dependence of the C₆H₆Ar⁺ ion is shown in Fig. 1, but the ion (C₆H₆)₂Ar₂⁺ was not measured because its mass (m/e 236) is outside the range of this apparatus. From Tables I(f) and I(g), it is evident that again very similar center line energies and widths are found, especially for the more energetic ions. Their behaviors are compatible with the Kamke et al. interpretation by requiring that the narrow peaks originate from a lone Ar atom on one side of the benzene molecule and the wide peaks have their source in two or more Ar atoms on the same side of the benzene molecule.

The largest clusters examined were C₆H₆Ar₃+, (C₆H₆)₂Ar₂, and (C₆H₆)₂Ar₃, which yield the ions C₆H₆Ar₃⁺ and (C₆H₆)₂Ar²⁺ on direct or dissociative photoionization, respectively. Behavior of the wide peaks as a function of nozzle pressure is given in Tables I(h) and I(i). From experience with the smaller ions, it is anticipated that C₆H₆Ar₂ and (C₆H₆)₂Ar₃ are involved in an analogous way with the production of narrow and wide peaks. Here, the sources of narrow and wide peaks are comparable at about 600 Torr (see Fig. 8). The ion C₆H₆Ar₃⁺ (m/e 198) could be seen, although only at low intensity.

In neither of these cases were the narrow peaks detected, even at the lowest nozzle pressures. This is similar to observations for (C₆H₆)₂Ar⁺ and again may indicate that the Ar atom responsible for Penning ionization is embedded in the cluster.

Finally, we note that searches for simultaneous excitation of two argon atoms were unsuccessful.

CONCLUSIONS

Although the PES of the benzene-argon system is well understood, there is much to be learned about complexes that include more than one argon atom or more than one benzene molecule. A promising technique is the study of intracluster Penning ionization from the (3p)(4s)¹ Rydberg states of the bound argon. One finding is that for complexes of a single benzene molecule, the line positions and widths of the atomic Ar Rydberg ionization states change very little with the number of bound argon atoms, at least up to three argon atoms. For the complex containing two benzene molecules, the lines attributed to binding of an argon atom to the face of a single benzene molecule disappeared. Instead, only lines of slightly higher energy and which are much broader persist. They are associated with a complex in which argon is embedded in the cluster as [(1)]. As the cluster size grows, the line positions and widths continue to show virtually no change, suggesting that multiple Ar atoms tend to cluster together on the same side of the benzene.

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