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# Argon matrix photolysis and photoionization studies of benzene. Absorption spectrum of benzene cation and benzene dimer cation

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Argon/benzene samples subjected to argon resonance photoionization during condensation at  $21 \pm 1$  K revealed sharp  $C_2^-$  and 552.5 nm bands, a broad absorption at 900 nm, and broad peaks at 502, 488, 474 nm coalescing into unstructured absorption extending to about 420 nm. The latter absorptions were destroyed and the  $C_2^-$  absorptions decreased by photolysis which suggests molecular cation assignments. The broad 900 nm absorption is in agreement with an earlier assignment to the intervalence transition in  $(C_6H_6)_2^+$ . Near agreement between the 552.5 nm absorption energy and the difference between the sharp origins for the first two benzene photoelectron bands suggests tentative assignment of the sharp, weak 552.5 nm band to the vibronically allowed  ${}^2E_{2g} + e_{2u} \leftarrow {}^2E_{1g}$  transition of  $C_6H_6^+$ . The stronger broad, structured absorption beginning at 502 nm could be due to the allowed  ${}^2A_{2u} \leftarrow {}^2E_{1g}$  absorption of  $C_6H_6^+$ . A strong 310 nm band system, which decreased on photolysis, is assigned to the  $C_6H_7$  radical; 288 and 534 nm absorptions produced by photolysis are attributed to the  $C_6H_5$  radical.

## INTRODUCTION

Absorption spectra of molecular ions in noble gas matrices complement gas-phase studies of ions and often provide additional information. In an important matrix study of the vacuum-ultraviolet photolysis of  $C_2H_2$ , Milligan and Jacox<sup>1</sup> found that doping the sample with cesium atoms markedly enhanced new argon matrix absorptions, which substantiated their attribution to the  $C_2^-$  species. The close agreement between the matrix spectrum and the gas-phase spectrum<sup>2</sup> tentatively assigned to  $C_2^-$  confirmed the gas-phase assignment. Andrews and Prochaska observed the absorption spectrum of  $CCl_4^+$  trapped in solid argon<sup>3</sup>; however, due to its instability to chlorine atom elimination, this photo-sensitive parent cation has not yet been detected in the gas phase. The absorption spectra of  $CH_2Cl_2^+$ ,  $CH_2Br_2^+$ , and  $CH_2I_2^+$  in solid argon<sup>4</sup> correspond to the energy differences between the first and a higher band in photoelectron spectra of the precursors,<sup>5</sup> which reinforces the identification of the parent cations in solid argon. Bondybey *et al.* studied the strong laser-induced fluorescence excitation spectrum of hexafluorobenzene cation and found excellent agreement with the gas-phase spectrum.<sup>6</sup> Since the quantum yield for fluorescence from difluorobenzene cation is substantially lower than from  $C_6F_6^+$ , it is not surprising that fluorescence from benzene cation has not been observed in the gas phase.<sup>7</sup> The failure to observe fluorescence from the  ${}^2A_{2u}(\pi)$  excited state of benzene cation has been rationalized as being due either to rapid internal conversion to the  ${}^2E_{2g}(\sigma)$  state whose transition to the ground state is dipole forbidden,<sup>7</sup> or because of internal conversion to excited vibrational levels of the ground  ${}^2E_{1g}(\pi)$  state (from which a second photon may photodissociate benzene cation).<sup>8</sup>

Benzene is of much chemical interest, and the benzene radical cation ( $C_6H_6^+$ ) has been studied quite extensively by many experimental and theoretical techniques, as summarized in a recent report.<sup>9</sup> Vacuum-ultraviolet absorption spectra of benzene have identified

Rydberg series leading to adiabatic ionization energies of 9.25, 11.49, and 16.84 eV.<sup>10</sup> Photoelectron spectra exhibited structured bands at these energies.<sup>11-15</sup> The first ionization at 9.25 eV clearly corresponds to removal of an electron from the highest occupied  $\pi$  level, the doubly degenerate  $1e_{1g}$  orbital of the molecule. However, there is disagreement between orbital assignments of the photoelectron spectra<sup>11-13,15</sup> and calculated orbital energies for benzene<sup>9,16-19</sup> as to whether the assignment of the second ionization should be to the lower  $\pi$  level  $1a_{2u}$  or to the highest-occupied  $\sigma$  orbital  $3e_{2g}$ . Current discussions outline arguments for each assignment but neither is compelling; calculations now place the two orbitals in question within about 0.3 eV.<sup>9</sup>

Absorption spectra assigned to benzene cation following  $\gamma$  radiolysis of glassy benzene solutions at 77 K<sup>20</sup> have been reassigned to the intervalence transition in the benzene dimer cation  $[C_6H_6]_2^+$  and an absorption at  $18\,000\text{ cm}^{-1}$  in more dilute samples has been attributed to benzene cation.<sup>21</sup> The subject of intervalence transitions in species like benzene dimer cation is itself of considerable interest.<sup>22-24</sup> The identification<sup>25</sup> of benzene cation from a structured 560-450 nm absorption in the solid bombarded by sodium atoms and/or ions has been questioned and a case made for reassignment of the visible band system to cyclohexadienyl radical.<sup>26</sup> In order to obtain additional information on the absorption spectrum of benzene cation, argon matrix photoionization studies were performed on benzene, similar to those used to observe the visible spectrum<sup>3</sup> of  $CCl_4^+$  and infrared spectra of parent and daughter cations of the  $CF_3X$  precursors.<sup>27</sup>

## EXPERIMENTAL

The experimental apparatus for optical absorption studies and the windowless discharge resonance lamps have been described previously.<sup>28,29</sup> Samples of benzene (Aldrich, c.p., triple distilled, dried over sodium) and benzene- $d_6$  (Aldrich, 99%) in argon (Ar/Bz = 50/1

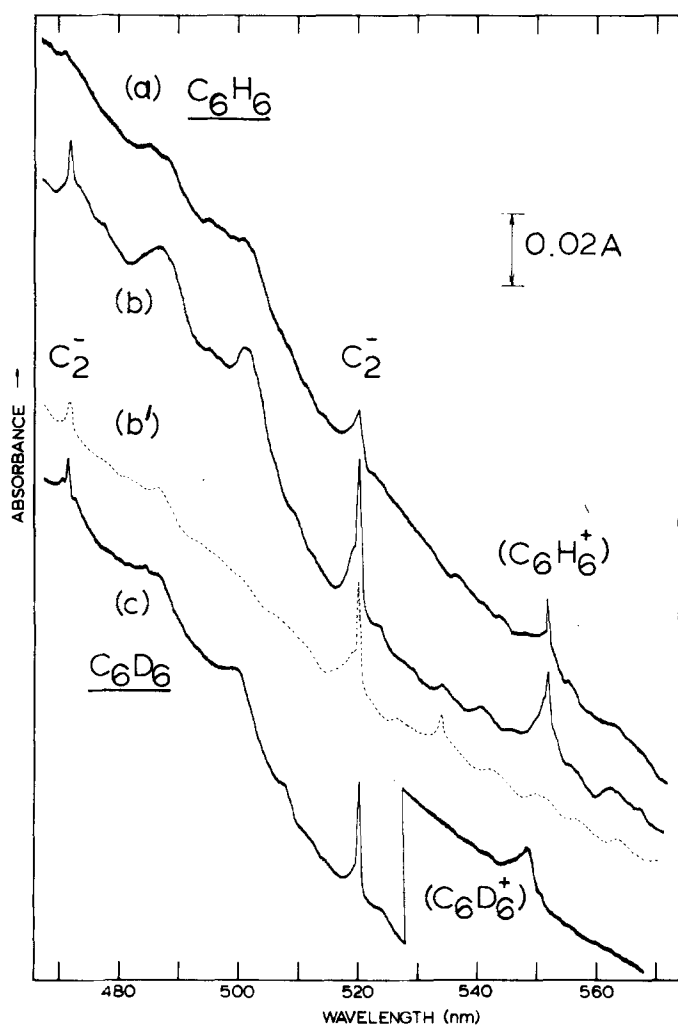


FIG. 1. Visible spectra recorded on 0.1 absorbance range for argon/benzene samples deposited at  $21 \pm 1$  K during simultaneous irradiation from a 3 mm orifice argon discharge lamp for 6–8 h. Samples diluted approximately twofold by argon from the discharge. (a) Ar/Bz = 200/1, (b) Ar/Bz = 100/1, (b') dashed trace recorded after 220–1000 nm mercury arc photolysis for 30 m, (c) Ar/C<sub>6</sub>D<sub>6</sub> = 100/1.

to 200/1) were condensed at about 0.4 to 1.0 mM/h on a sapphire plate at 20–22 K with simultaneous irradiation from the argon discharge lamp with argon flowing through the discharge tube at about 1 mM/h; adjustment of these flow rates was critical to obtain good sample transmission for the 4–8 h sample deposition periods required. Spectra were recorded from 200–1400 nm on a Cary 17 recording spectrophotometer. Some samples were doped with CCl<sub>4</sub> which was intended to serve as an electron scavenger. After preparation, a number of samples were photolysed by a filtered high-pressure mercury arc (BH-6-1, Illumination Industries, Inc.) and additional spectra were recorded.

## RESULTS

Twenty-five optical matrix photoionization studies were performed on benzene systems to determine the best conditions for producing new product absorptions. Figure 1, trace (a), shows a portion of the spectrum

from 570 to 470 nm recorded on the 0.1 absorbance range for an Ar/Bz = 200/1 experiment using a 3 mm orifice discharge lamp for 8 h, and the product absorptions are summarized in Table I. The most interesting new feature is the sharp band at 552.5 nm ( $A = 0.016$ , FWHM = 15 cm<sup>-1</sup>). The sharp absorptions observed at 520.7 and 472.6 nm are clearly C<sub>2</sub><sup>-</sup> bands.<sup>1</sup> Weak broad absorptions appeared at 564, 502, 488, and 474 nm. A sharp strong band system was also observed at 310 nm ( $A = 0.1$  after 4 h) and weak bands were also observed at 409, 396, and 385 nm. Finally, a weak, broad band appeared between 800 and 1000 nm ( $A = 0.02$ ).

Similar experiments were performed with Ar/Bz = 100/1 samples, and the product absorptions were more intense. Figure 1(b) illustrates spectra for the sharp new bands. The 552.5 nm band ( $A = 0.020$ ) exhibits a shoulder at about 549.5 nm. The sharp C<sub>2</sub><sup>-</sup> bands had  $A = 0.044$  and 0.013, respectively. Behavior of the product absorptions after photolysis for 30 m with 220–1000 nm radiation is summarized in Table I. Photolysis destroyed the 552.5 nm band, markedly decreased the broad 502 and 488 nm bands, and reduced the C<sub>2</sub><sup>-</sup> bands by 25%, as is shown in the dashed trace of Fig. 1(b'). Experiments were also performed with Ar/Bz = 200/1 samples using different sized orifice discharge lamps. The open tube (8 mm i.d.) produced a slightly weaker product spectrum than shown in Fig. 1(a); the 1 mm orifice tube failed to give detectable products.

Four experiments were performed with C<sub>6</sub>D<sub>6</sub> samples using the 3 mm orifice tube; the spectrum from the first 100/1 study is shown in Fig. 1(c). The sharp, new product feature shifted and exhibited a sharp peak at 549.3 nm ( $A = 0.014$ ) with a broad shoulder at 548.7 nm, and the C<sub>2</sub><sup>-</sup> bands were unshifted. Weak, broad bands were observed at 564, 500, 487, 472, and 900 nm ( $A = 0.03$ ). The structured ultraviolet band origin was displaced to 308 nm and three weak bands were shifted to 407, 394, 382 nm. After 45 m of 220–1000 nm photolysis, the 549 nm band and the near infrared band were destroyed, the broad visible features were decreased substantially and the C<sub>2</sub><sup>-</sup> absorptions were reduced by 20%. A 200/1 C<sub>6</sub>D<sub>6</sub> study yielded weaker product features.

Another 100/1 C<sub>6</sub>D<sub>6</sub> experiment gave similar product bands whose photolysis behavior at different wavelengths is contrasted with corresponding C<sub>6</sub>H<sub>6</sub> spectra in the 520–560 and 280–320 nm regions in Fig. 2. Deuterium shifts were observed for many of the product absorptions listed in Table I. Photolysis of the C<sub>6</sub>H<sub>6</sub> sample in Fig. 2(a) with 290–1000 nm light for 90 m caused a 20% reduction in the sharp 552.5, 520.7, and 472.6 nm absorptions and reduction from  $A = 0.7$  to  $A = 0.4$  in the 310 nm band as illustrated in Fig. 2(b); a subsequent 30 m photolysis with 220–1000 nm radiation destroyed the 552.5 nm band, slightly decreased the C<sub>2</sub><sup>-</sup> absorptions, reduced the 310 nm absorption to  $A = 0.17$  and produced bands at 288 nm ( $A = 0.4$ ) and 534 nm ( $A = 0.005$ ) as shown in Fig. 2(c). Photolysis of the C<sub>6</sub>D<sub>6</sub> sample in Fig. 2(d) with 290–1000 nm light for 30 m slightly increased the C<sub>2</sub><sup>-</sup> absorptions, decreased the 549 nm band from  $A = 0.008$  to  $A = 0.005$  and the

TABLE I. Product absorptions (nm) for argon resonance photoionization experiments with benzene matrix systems.

C <sub>6</sub> H <sub>6</sub> Product abs	Identification	Physical behavior	C <sub>6</sub> D <sub>6</sub> Product abs	Identification
900	(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub> <sup>a</sup>	a	900	(C <sub>6</sub> D <sub>6</sub> ) <sub>2</sub> <sup>a</sup>
656	?	b	...	...
564	?	b	564	?
552.5	(C <sub>6</sub> H <sub>6</sub> ) <sup>b</sup>	c	549.0	(C <sub>6</sub> D <sub>6</sub> ) <sup>b</sup>
534.3	C <sub>6</sub> H <sub>5</sub>	d	530.8, 531.5	C <sub>6</sub> D <sub>5</sub>
520.7, 472.6	C <sub>2</sub> <sup>c</sup>	e	520.7, 472.6	C <sub>2</sub> <sup>c</sup>
502, 488, 474	(C <sub>6</sub> H <sub>6</sub> ) <sup>d</sup>	c	500, 487, 472, ...	(C <sub>6</sub> D <sub>6</sub> ) <sup>d</sup>
453	(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub> <sup>a</sup>	a	...	...
409, 396, 385	?	b	407, 394, 382	?
310.2, 304.6, 299.8, 295	C <sub>6</sub> H <sub>7</sub>	b	308.5, 303, ..., 293	C <sub>6</sub> D <sub>7</sub>
288	C <sub>6</sub> H <sub>5</sub>	d	286	C <sub>6</sub> D <sub>5</sub>

<sup>a</sup>Favored in more concentrated samples and by sample condensation at higher temperature; destroyed by mercury arc photolysis.

<sup>b</sup>Decreased substantially [(70–80)%] by mercury arc photolysis.

<sup>c</sup>Destroyed by mercury arc photolysis.

<sup>d</sup>Increased by mercury arc photolysis.

<sup>e</sup>Decreased slightly [(20–30)%] by mercury arc photolysis.

308 nm band from  $A=0.25$  to  $A=0.12$ , as shown in Fig. 2(e). The spectrum after final 220–1000 nm photolysis in Fig. 2(f) shows slight reduction of the sharp C<sub>2</sub> bands, complete destruction of the 549 nm absorption, reduction of 308 nm to  $A=0.03$ , and production of a sharp new 530.8, 531.5 nm doublet and a strong 286 nm absorption.

In searching for optimum experimental parameters, an Ar/Bz=100/1 sample was condensed at  $26 \pm 1$  K with simultaneous irradiation from the 3 mm discharge lamp using a slower argon flow rate through the lamp. The broad 900 nm absorption was more intense ( $A=0.10$ ), a weak broad band was found at 453 nm ( $A=0.015$ ) and no other product absorptions were observed, as illustrated in Fig. 3(b). Another 100/1 experiment performed with the substrate at  $21 \pm 1$  K is contrasted in Fig. 3(a). The broad 900 nm band was reduced ( $A=0.03$ ), but the product features described above in the visible region were observed.

An identical 100/1 C<sub>6</sub>H<sub>6</sub> experiment was performed using Ar/H<sub>2</sub>=100/1 as the discharge gas to add reactive hydrogen atoms to the matrix system. The spectrum was similar to those in Figs. 1(b) and 2(a) with typical yields of all product species. In addition, three weak sharp bands were observed at 627, 568, and 515 nm ( $A=0.03$ ).

Several benzene experiments were also performed with CCl<sub>4</sub> added to serve as an electron scavenger and to provide a positive ion capable of resonant charge transfer with benzene.<sup>20</sup> The most successful study employed an Ar/Bz/CCl<sub>4</sub>=400/4/1 sample and the 3 mm orifice tube for a 3 h deposition period. The very strong 425 nm CCl<sub>4</sub> absorption<sup>3</sup> ( $A \approx 3$ ) obtained thereby was almost entirely destroyed by 340–600 nm photolysis

with the sample warmed to 32 K. The spectrum yielded the very broad 900 nm near infrared band ( $A=0.06$ ), a 564 nm absorption, a sharp, weak 552 nm band and three bands at 502, 488, and 474 nm. A final 220–1000 nm photolysis destroyed the 552 and 564 nm absorptions and slightly reduced the near infrared and 502, 488, and 474 nm bands.

Similar experiments were done with 200/1 samples of toluene and chlorobenzene. The latter precursor produced a broad, weak band with a maximum at 472 nm which was reduced by 290–1000 nm photolysis and destroyed by 220–1000 nm radiation. An additional weak series was observed at 410, 402, and 390 nm. The former precursor gave a weak, sharp 449.5 nm band, broad weak 430 and 317 nm absorptions, and a strong, sharp 310.5 nm band; the broad, weak bands were destroyed on photolysis. Neither substituted benzene precursor gave a product absorption at 520 or 552 nm.

Two final optical studies employed a conventional resonance lamp with a MgF<sub>2</sub> window, similar to that used by Milligan and Jacox,<sup>1</sup> and a 5% H<sub>2</sub> mixture in argon powered by a microwave discharge. Samples of Ar/Bz=200/1 were deposited for 2 h periods, then irradiated *in situ* for 10–20 m periods and this cycle was repeated twice. The optical spectra in both experiments revealed only the 310 nm band with reduced intensity ( $A=0.01$ ).

An infrared experiment was performed with the apparatus described earlier<sup>27</sup> on an Ar/Bz=400/1 sample using the 3 mm tube for 20 h. Product absorptions included strong C<sub>2</sub>H<sub>2</sub> bands at 737 cm<sup>-1</sup> ( $A=0.7$ ) and 3303, and 3289 cm<sup>-1</sup> ( $A=0.1$ ), weak C<sub>2</sub>H<sub>4</sub> absorption at 949 cm<sup>-1</sup>, and new bands at 707, 771, 926, and 1343 cm<sup>-1</sup>

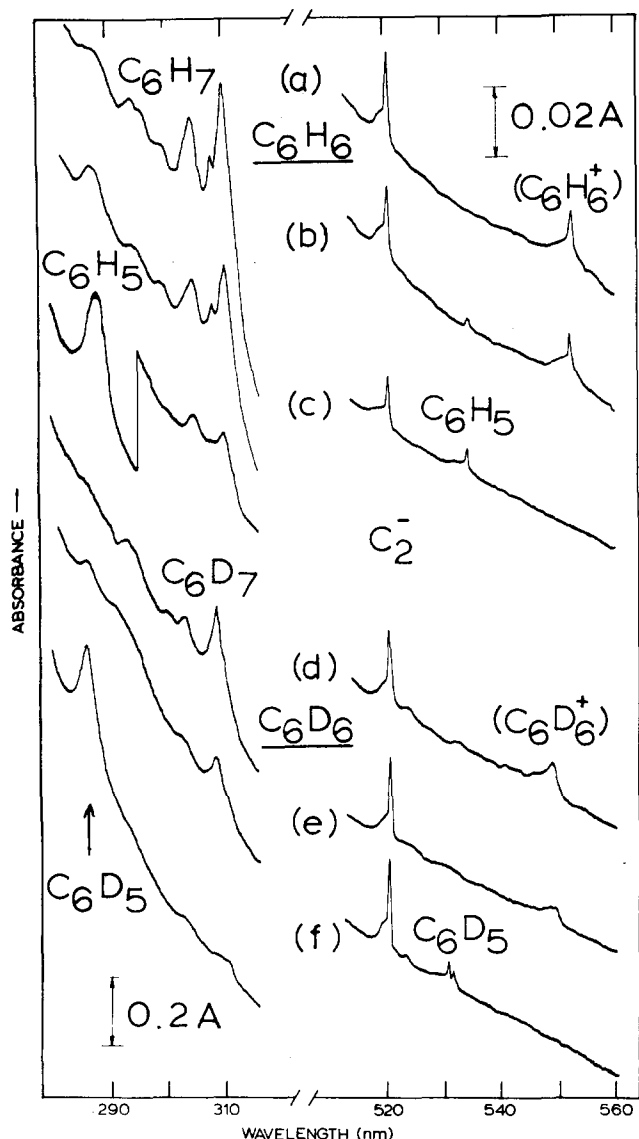


FIG. 2. Ultraviolet and visible spectra of argon/benzene samples condensed at  $21 \pm 1$  K with argon discharge radiation. (a)  $\text{Ar}/\text{C}_6\text{H}_6 = 100/1$ , (b) after 290–1000 nm photolysis for 90 m, (c) after 220–1000 nm photolysis for 30 m, (d)  $\text{Ar}/\text{C}_6\text{D}_6 = 100/1$ , (e) after 290–1000 nm photolysis for 30 m, (f) after 220–1000 nm photolysis for 30 m. Ultraviolet spectra recorded on 1.0 absorbance range, visible spectra recorded on 0.1 absorbance range. Bands are labelled in accord with discussion in the text.

( $A = 0.1$ ). Photolysis for 1 h with 220–1000 nm radiation increased the  $707\text{ cm}^{-1}$  band (to  $A = 0.13$ ) and had no effect on the other product absorptions. An identical experiment was performed without discharge photolysis to identify benzene sample bands.

## DISCUSSION

The optical absorption spectra will be considered for possible assignments to neutral and charged photolysis products of benzene.

### Identification of free radicals

Electron spin resonance studies of solid benzene<sup>30</sup> and benzene in alcohols<sup>31</sup> at 77 K subjected to radiolysis

have identified the major product free radicals as cyclohexadienyl ( $\text{C}_6\text{H}_7$ ) and phenyl ( $\text{C}_6\text{H}_5$ ) with the latter more stable on sample warming. The strong structured absorption beginning at 310 nm in solid argon has similar spacing and relative intensities and is in near agreement with the 316 nm absorption in  $\text{CH}_3\text{OH}$  assigned to the  $\text{C}_6\text{H}_7$  radical.<sup>32–34</sup> Its steady photodissociation with mercury arc radiation is consistent with a radical of limited stability. Accordingly, the strong 310 nm matrix absorption, which shows a  $190\text{ cm}^{-1}$  blue deuterium shift in agreement with the radiolysis work, is assigned to the  $\text{C}_6\text{H}_7$  radical. The  $560 \pm 40\text{ cm}^{-1}$  spacing is probably due to a ring vibrational mode. Although benzyl radical also absorbs at 310 nm,<sup>35</sup> the strong 310 nm absorption in benzene studies shows a markedly different photolysis behavior and different vibrational structure from the single, very sharp 310 nm absorption in toluene experiments. The toluene product absorption is due to benzyl radical, as will be described in a later report.<sup>36</sup>

Without reviewing the Shida–Duley controversy,<sup>25,26</sup> consideration of the sample preparation methods of both groups, and the present experiments together suggest that the  $\text{C}_6\text{H}_7$  identification of the earlier structured 559 nm absorption is correct. Although the evidence indicates that the 310 nm argon matrix absorption in the present benzene experiments is due to  $\text{C}_6\text{H}_7$ , the 300-fold weaker  $\text{C}_6\text{H}_7$  visible band system<sup>34</sup> has not been observed in the present matrix work. Counterparts of the two strongest vibronic components in the weak  $\text{C}_6\text{H}_7$  band system with intensities near half of the origin band were not observed here which rules out assignment of the single 552 nm band to the weak visible band system of  $\text{C}_6\text{H}_7$ .

Photolysis experiments were performed to determine if the strong 310 nm and the sharp 552 nm absorptions could be due to the same molecular species. The spectra in Fig. 2 conclusively show that this is not the case. Pyrex-filtered photolysis (290–1000 nm) substantially reduced the 310 nm band with only a slight reduction at 552 nm, and the full arc (220–1000 nm) totally destroyed the 552 nm band leaving about 25% of the 310 nm absorption. Similar behavior was observed for the deuterium counterparts at 308 and 549 nm. The different photolysis behaviors of the 552 and 310 nm bands demonstrate that these two absorptions are due to different species.

Mercury arc photolysis markedly reduced the strong 310 nm  $\text{C}_6\text{H}_7$  radical absorption and produced a strong 288 nm band and a sharp, weak 534.3 nm absorption, as shown in Fig. 2. These new product bands exhibited deuterium shifted counterparts at 286 and 530.8 nm. The 288 nm matrix absorption is in reasonable agreement with the 260 nm ultraviolet band assigned to phenyl radical in aqueous solutions,<sup>37</sup> which suggests assignment of the 288 nm argon matrix photolysis product to  $\text{C}_6\text{H}_5$  radical. Phenyl radical can be produced in these experiments by photoelimination of an  $\text{H}_2$  molecule from  $\text{C}_6\text{H}_7$  (or by dissociation of  $\text{C}_6\text{H}_6$ ) with the full mercury arc (220–1000 nm). The sharp 534.3 nm ( $18\,716\text{ cm}^{-1}$ ) argon matrix absorption is in excellent agreement with the  $18\,908\text{ cm}^{-1}$  origin for the structured

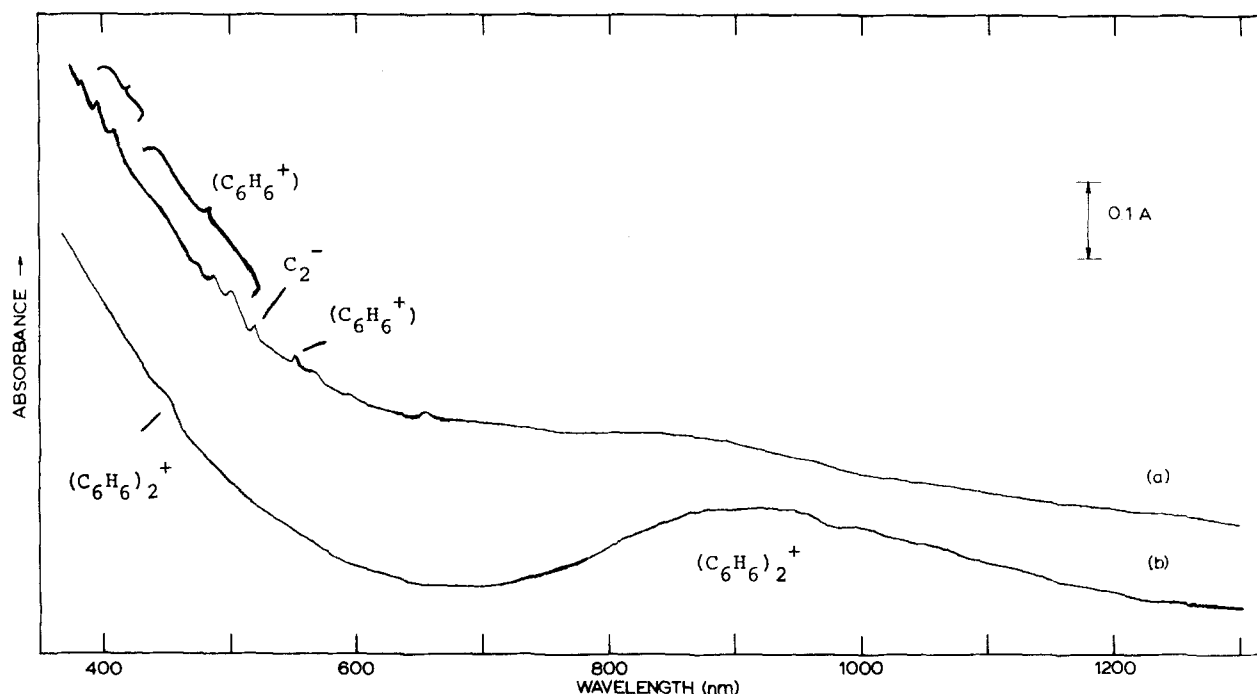


FIG. 3. Near infrared and visible spectra of argon/benzene=100/1 samples subjected to argon resonance photoionization during condensation. (a) Sample condensation at  $21 \pm 1$  K, argon flow through discharge about 1 mM/h; (b) sample condensation at  $26 \pm 1$  K, argon flow through discharge about 0.5 mM/h.

absorption of phenyl radical produced by flash photolysis of benzene vapor.<sup>38</sup> A  $192\text{ cm}^{-1}$  matrix shift to lower energy is reasonable for this phenyl radical transition.

The infrared product band at  $707\text{ cm}^{-1}$ , which increased 30% on photolysis, is in excellent agreement with the  $710\text{ cm}^{-1}$  assignment to the out-of-plane bending mode of phenyl radical produced by photolysis of acetyl benzoyl peroxide.<sup>39</sup> This infrared observation of phenyl radical in similar experiments supports the above optical assignments to phenyl radical.

#### Identification of molecular ions

In addition to the cyclohexadienyl and phenyl radicals, charged species were produced and trapped in the present experiments. The continuous open discharge matrix photoionization technique employed here was developed to produce daughter cations from free radical photolysis products for infrared absorption study.<sup>27</sup> This method gives a higher total yield of product species with less selective formation of ions than brief *in situ* hydrogen resonance photoionization through LiF as employed by other co-workers.<sup>6</sup> The present method is capable of producing and trapping a larger total number of ions, and if these absorptions can be sorted from those of neutral fragments, useful spectroscopic data can be obtained for molecular ion products.

The  $\text{C}_2^-$  anion was produced in substantial yield, as identified by sharp 520.7 and 472.6 nm absorptions.<sup>4</sup> This observation of  $\text{C}_2^-$  demonstrates that photoionization occurs in these samples. Argon resonance lines at 11.6 and 11.8 eV from the windowless resonance lamp<sup>29</sup> are sufficient to photoionize benzene.<sup>13</sup> The  $\text{C}_2^-$  species serves as an electron trap in these experiments; such a

trap is necessary for positively charged species to survive sample condensation.

Ion photochemistry in these samples is complicated and depends on which wavelength range is employed first. With 290–1000 nm radiation,  $\text{C}_2^-$  has been observed to increase and to decrease up to 20% in different experiments suggesting that electrons are photodetached from traps with this radiation<sup>40</sup> both forming and destroying  $\text{C}_2^-$ . The 25% reduction of the 552.5 nm absorption with 290–1000 nm photolysis is probably due to neutralization by these photoelectrons. Continued 220–1000 nm photolysis had little effect on the  $\text{C}_2^-$  absorptions, but in every experiment, the 552 nm (or 549 nm in  $\text{C}_6\text{D}_6$  runs) and 900 nm bands were completely destroyed. This suggests a different mechanism for photolysis with 220–290 nm radiation, perhaps photodissociation of the ion itself, which is consistent with the single photon dissociation of  $\text{C}_6\text{H}_6^+$  peaking at 255 nm in ICR experiments.<sup>8</sup> Complete photolytic destruction is characteristic of parent cations in a number matrix isolation studies.<sup>3,4,27</sup> In support of this finding,  $\text{C}_6\text{F}_6^+$ , as monitored by its absorption spectrum which agreed with the excitation spectrum of Bondybey *et al.*,<sup>6</sup> was virtually completely destroyed by 220–1000 nm photolysis in similar studies in this laboratory. The photolysis behavior of the 552 and 900 nm bands is distinctive; total photodestruction strongly suggests that these bands are due to parent cations.

The weak, broad band ranging from 800–1000 nm and centered at 900 nm exhibited an increase in intensity relative to the sharp 552.5 nm absorption when benzene concentration in the sample was increased. This near infrared band was destroyed on photolysis along with the

sharp 552.5 nm band. In the experiment performed on a  $26 \pm 1$  K substrate, the 900 nm absorption was enhanced and a new weak, broad band was observed at 453 nm; however, the other product absorptions in the visible region were not seen. The  $\text{CCl}_4$ -doped benzene experiment also produced an increased yield of the 900 nm band. A strong 925 nm absorption was produced by radiolysis of benzene in a *n*-butyl chloride-isopentane glass at 77 K and assigned to the intervalence transition of benzene dimer cation.<sup>21</sup> The argon matrix observations are consistent with assignment of the 900 nm band to  $(\text{C}_6\text{H}_6)_2^+$ . In fact the present observation of the 900 nm band in a nonpolar medium supports its earlier identification as  $(\text{C}_6\text{H}_6)_2^+$ . The weak 453 nm argon matrix band corresponds to the much weaker benzene dimer cation band at 465 nm in the low-temperature glass.

The intervalence transition in  $(\text{C}_6\text{H}_6)_2^+$  is of considerable theoretical interest. This dimer cation is an especially simple prototype of the symmetrical ( $A=B$ ) case described in a recent vibronic coupling model of mixed valence systems.<sup>22-24</sup>  $(\text{C}_6\text{H}_6)_2^+$  has an appealing simplicity and does not contain the mixed valence (multiple oxidation state) metal atoms so often associated with such species. It was our hope in preparing this species to resolve vibronic structure in the intervalence band and to provide an interesting test of the vibronic theory which claims the ability to predict the position and relative intensity of the most important progression in such a band.<sup>22-24</sup> A low-temperature "inert" matrix environment seemed well suited for such observation, but no vibronic structure was observed. Such investigations are continuing with related molecular species. In addition, the vibronic coupling model<sup>23</sup> predicts low-energy "tunneling" transitions in such systems whose observation would again provide an important test of the theory. In the case of  $(\text{C}_6\text{H}_6)_2^+$ , such a transition is predicted to occur in the far infrared at  $\sim 265$   $\text{cm}^{-1}$  with an integrated intensity about 40% that of the 900 nm intervalence band.<sup>24</sup> Studies are underway in an attempt to observe this predicted transition, which has recently been observed in the mid-infrared region for a diketone mixed-valence anion radical.<sup>41</sup>

The sharp  $552.5 \pm 0.1$  nm ( $18\,100 \pm 3$   $\text{cm}^{-1}$ ) absorption is most intriguing because it fits the  $2.245 \pm 0.004$  eV ( $18\,108 \pm 32$   $\text{cm}^{-1}$ ) energy difference between the first two sharp photoelectron band origins for benzene.<sup>10,14,41,43</sup> Photoelectron spectra are useful for predicting optical transition energies; emission band origins for a number of fluorine substituted benzene cations in the gas phase agree to  $\pm 0.03$  eV (240  $\text{cm}^{-1}$ ) with the difference between the appropriate ionization energies.<sup>7</sup> The deuterium counterpart of the sharp 552.5 nm argon matrix band exhibited split components at 549.3 and 548.7 nm measured relative to the sharp  $\text{C}_7^+$  absorption; the band center,  $549.0 \pm 0.1$  nm ( $18\,215 \pm 3$   $\text{cm}^{-1}$ ), represents the best measure of the deuterium shift ( $18\,215 \pm 3 - 18\,100 \pm 3 = 115 \pm 6$   $\text{cm}^{-1}$ ).

The first ionization of benzene at 9.25 eV results in the removal of an electron from the highest-occupied doubly degenerate  $\pi$  level giving a  ${}^2E_{1g}$  ground state for

$\text{C}_6\text{H}_6^+$ . Since both the  ${}^2E_{2g}(\sigma)$  and  ${}^2A_{2u}(\pi)$   $\text{C}_6\text{H}_6^+$  excited states are known from PES<sup>13</sup> to be in the appropriate energy region, about 2.2–2.9 eV above the ground state ion, a straightforward interpretation of the matrix absorption is to the dipole-allowed  ${}^2A_{2u} \leftarrow {}^2E_{1g}$  transition of benzene cation. This possible assignment would indicate that the sharp 11.49 eV ionization produces the  ${}^2A_{2u}$  state as originally proposed by the Turner group<sup>11-13</sup> since  $(11.49 - 9.25 \text{ eV}) = 18\,076$   $\text{cm}^{-1}$ , in excellent agreement with the sharp 18 100  $\text{cm}^{-1}$  matrix absorption.

However, two points argue against this possible assignment. First, the blue deuterium shift,  $115 \pm 6$   $\text{cm}^{-1}$ , for the sharp matrix band is somewhat smaller than the  $194 \pm 64$   $\text{cm}^{-1}$  blue shift deduced for the gaseous ion from the most accurate ionization energy data available ( $2.269 \pm 0.004$  eV for the  $\text{C}_6\text{D}_6^+$  transition minus  $2.245 \pm 0.004$  eV for the  $\text{C}_6\text{H}_6^+$  transition).<sup>10,14,15,42,43</sup> The deuterium shift data probably rule out assignment of the sharp matrix band to the vibrationless transition between the first two states of  $\text{C}_6\text{H}_6^+$ . Finally, the bulk of recent physical evidence places the  ${}^2A_{2u}$  state 2.5–3.0 eV above the ground state ion.<sup>9</sup> Gas-phase fluorescence studies on fluorine substituted benzene cations give a 48 ns radiative lifetime and unit quantum yield for  $\text{C}_6\text{F}_6^+$  and predict a quantum yield of  $< 10^{-5}$  for  ${}^2A_{2u}$   $\text{C}_6\text{H}_6^+$ , which imply a  $< 10^{-12}$  s lifetime for  $\text{C}_6\text{H}_6^+$  in the optically allowed  ${}^2A_{2u}$  state.<sup>7</sup> This is in accord with the presently accepted assignment of the broad 12.1 eV PES band as being due to ionization from the  $a_{2u}$  orbital of  $\text{C}_6\text{H}_6^+$ . These arguments predict a broad absorption spectrum for the  $\text{C}_6\text{H}_6^+$  transition terminating in the  ${}^2A_{2u}$  state. The presence of the dipole-forbidden  ${}^2E_{2g}$  state at lower energy is necessary if the nonradiative path is to dominate the depletion of the  ${}^2A_{2u}$  state in  $\text{C}_6\text{H}_6^+$ .

The forbidden origin of the  ${}^2E_{2g} \leftarrow {}^2E_{1g}$  transition is expected near 18 108  $\text{cm}^{-1}$  in the gas phase from PES measurements.<sup>10,14,15,42,32</sup> This electronic transition is vibronically allowed via an  $e_{2u}$  vibrational mode; neutral benzene has such a mode,  $\nu_{20}(e_{2u})$ , at 404  $\text{cm}^{-1}$  with a deuterium counterpart at 337  $\text{cm}^{-1}$ .<sup>44</sup> Progressions involving the  $\nu_{20}(e_{2u})$  vibration were found to be associated with the Rydberg transitions of  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{D}_6$  leading to the first ionization limit.<sup>42</sup> This vibration has values of 314  $\text{cm}^{-1}$  for  $\text{C}_6\text{H}_6$  and 262  $\text{cm}^{-1}$  for  $\text{C}_6\text{D}_6$  which should provide reasonable estimates for the  $\nu_{20}(e_{2u})$  mode of the  ${}^2E_{2g}$  state of  $\text{C}_6\text{H}_6^+$ . A plausible model predicts the vibronic origin,  $0 + \nu_{20}$ , at  $18\,108 \pm 32 + 314 = 18\,422 \pm 32$   $\text{cm}^{-1}$  in the gas phase, in reasonable agreement with the sharp, weak 18 100  $\text{cm}^{-1}$  matrix absorption. The implied red matrix shift of 322  $\text{cm}^{-1}$  is near the 234  $\text{cm}^{-1}$  gas-to-argon matrix shift<sup>6</sup> found for  $\text{C}_6\text{F}_6^+$ .

The deuterium isotopic data are also in qualitative accord with a possible vibronic  $\text{C}_6\text{H}_6^+$  assignment for the sharp matrix band. The vibronic origin for  $\text{C}_6\text{D}_6^+$  is predicted from the Rydberg series limit origin and the vibrational data to be  $18\,302 \pm 32 + 264 = 18\,566 \pm 32$   $\text{cm}^{-1}$  in the gas phase, which gives a blue deuterium shift of  $144 \pm 64$   $\text{cm}^{-1}$ , in reasonable agreement with the  $115 \pm 6$   $\text{cm}^{-1}$  blue deuterium shift for the matrix bands. Thus, the matrix blue shift is too low for the electronic origin



band, but it is appropriate for the vibronic origin. The Franck-Condon pattern, although somewhat unusual for a vibronic transition, resembles the 11.49 eV photoelectron band where vibronic intensity falls off rapidly.

The proposed  ${}^2E_{2g} + e_{2u} \rightarrow {}^2E_{1g}$  assignment for the weak 552.5 nm band requires stronger  $C_6H_6^+$  absorption in the 400–500 nm region for the allowed  ${}^2A_{2u} \rightarrow {}^2E_{1g}$  transition. Figure 3 indeed shows a broad photosensitive band beginning with weak structure at 502, 488 and 474 nm which coalesces into a broad unstructured absorption extending to about 420 nm. In the  $C_6D_6$  experiments the broad, weak structure is displaced to 500, 487 and 472 nm. All or part of this 500–420 nm absorption could be due to  $C_6H_6^+$ . Excitation of similar samples from 420 to 475 nm produced a broad, structured emission beginning at 19 770  $cm^{-1}$  which has been assigned to  $C_6H_6^+$  in solid argon.<sup>45</sup>

The first absorption band at 502 nm and the first emission band at 19 770  $cm^{-1}$  (506 nm) are in reasonable agreement in view of the 200  $cm^{-1}$  FWHM of each band and considering the contribution of lattice phonons to each band profile. This would thus place the zero-phonon band origin at approximately 504 nm. The second absorption band at 488 nm and the second emission band at 19 140  $cm^{-1}$  (522 nm) are each displaced from their respective origins by about  $600 \pm 30$   $cm^{-1}$ , which is appropriate for the Jahn-Teller active mode  $\nu_{18}$  ( $e_{2g}$ ) of  $C_6H_6^+$ . The third absorption peak discernible at 474 nm is also spaced by  $600 \pm 30$   $cm^{-1}$ . The  $\nu_{18}$  ( $e_{2g}$ ) mode is expected to be active in both the absorption and emission arising from the  ${}^2A_{2u} \rightarrow {}^2E_{1g}$  transition.<sup>14</sup> It must be pointed out that the  ${}^2A_{2u} \rightarrow {}^2E_{1g}$  absorption of benzene cation will not have the same Franck-Condon profile as the  ${}^2A_{2u}$  photoelectron band since the ground state ion is  $J-T$  distorted and the ground state molecule is symmetrical. In fact the  ${}^2A_{2u} \rightarrow {}^2E_{1g}$  absorption profile of  $C_6F_6^+$ , which has significant intensity at the origin,<sup>6,45</sup> is a possible model for this allowed absorption in  $C_6H_6^+$ .

The occurrence of both  ${}^2A_{2u}$  and  ${}^2E_{2g}$  states of  $C_6H_6^+$  in the 2.2–3.0 eV region can have a profound effect on the  $C_6H_6^+$  spectrum since the strong vibronic coupling of the  ${}^2E_{2g}$  and  ${}^2A_{2u}$  states via  $e_{2u}$  vibrations is expected to mix intensity into the vibronically allowed band ( ${}^2E_{2g} + \nu_{20} \rightarrow {}^2E_{1g}$ ). This is consistent with the rapid internal conversion postulated to explain the short fluorescence lifetime in the gas phase. However, the internal conversion rate in the lowest vibrational levels of the  ${}^2A_{2u}$  state will be reduced owing to a decreased density of vibrational states thus allowing the observation of broad vibrational structure near the origin in both the absorption and emission arising from the  ${}^2A_{2u} \rightarrow {}^2E_{1g}$  transition. Although a definitive assignment cannot be made, the photosensitive 502–420 nm absorption observed here could well be due to the allowed  $C_6H_6^+$  transition.

The radiolysis studies<sup>21</sup> of glassy benzene solutions produced a broad 18 000  $cm^{-1}$  band at low benzene concentrations, which was reduced on thermal cycling and at high concentrations, both conditions favoring the near infrared  $(C_6H_6)_2^+$  absorption. Accordingly, the 18 000  $cm^{-1}$  band was assigned to  $C_6H_6^+$ . This observation is compatible with the present suggested analysis of the

absorption spectrum of benzene cation under two possible circumstances: either the 18 000  $cm^{-1}$  glassy solution absorption is due to the vibronic transition with substantial intensity enhancement or is due to the allowed transition with an approximate 2,000  $cm^{-1}$  shift from the 502 nm argon matrix absorption.<sup>46</sup>

After all of these points are weighed, it is still possible that the sharp 552.5 nm absorption is due to another cation (like  $C_6H_5^+$ ), although daughter cations should be less abundant than parent cations in these experiments, or to a still unidentified photosensitive neutral species. The definitive observations of  $C_2^-$  and  $(C_6H_6)_2^+$  in these samples, the photosensitive nature of the sharp 552.5 nm band, the correlation with gas-phase PES for  $C_6H_6$  and the deuterium isotopic data show that a tentative assignment of the 552.5 nm band to the  ${}^2E_{2g} + e_{2u} \rightarrow {}^2E_{1g}$  vibronic transition of  $C_6H_6^+$  in solid argon is reasonable.

### Other absorptions

The weak structured series at 409, 396 and 385 nm decreased on photolysis and shifted to 407, 394 and 382 nm on deuteration. A presumably analogous series was observed in chlorobenzene experiments at 410, 402 and 390 nm. These bands could be due to photolysis products of less well-defined structure, perhaps benzene valence isomers or cations involving carbon-carbon bond rupture, which cannot be identified from the present data. The broad photosensitive bands at 430 and 472 nm in toluene and chlorobenzene experiments are due to the parent cations, respectively.<sup>36,47</sup>

### CONCLUSIONS

Matrix photoionization of argon/benzene samples during condensation at  $21 \pm 1$  K produced a sharp new product absorption at 552.5 nm, sharp  $C_2^-$  bands at 520.7 and 472.6 nm, broad bands at 502, 488 and 474 nm which coalesce into a broad unstructured absorption extending to about 420 nm, and a broad 900 nm absorption. The sharp product band shifted to 549.0, the broad bands shifted to 500, 487 and 472 nm and the  $C_2^-$  bands were unchanged in similar  $C_6D_6$  experiments. The 552.5, 502, 488, 474 and 900 nm absorptions were destroyed and the  $C_2^-$  bands were reduced by mercury arc photolysis which suggests that the former absorptions are due to molecular cations. Earlier radiolysis work shows that the 900 nm band is due to the intervalence transition of  $(C_6H_6)_2^+$ . The sharp 552.5 nm absorption is in near agreement with the energy difference between the first two  $C_6H_6$  photoelectron bands. Considering the gas-phase PES and fluorescence work on substituted benzene cations, a reasonable assignment of the sharp matrix band is to the vibronic transition  ${}^2E_{2g} + e_{2u} \rightarrow {}^2E_{1g}$  of  $C_6H_6^+$ , and the broad 502, 488 and 474 nm bands could be due to the allowed absorption  ${}^2A_{2u} \rightarrow {}^2E_{1g}$  of  $C_6H_6^+$  in solid argon.

A strong 310 nm band system is assigned to the  $C_6H_7$  radical in agreement with radiolysis studies, and absorptions at 288 and 534 nm produced by photodissociation of  $C_6H_7$  are attributed to the  $C_6H_5$  radical on the basis of comparison with earlier work.



*Note added in proof:* An alternative explanation for the benzene cation absorption and emission<sup>45</sup> spectra is provided by interaction with the argon matrix such that the  ${}^2A_{2u}(\pi)$  and  ${}^2E_{2g}(\sigma)$  excited state energies are reversed. The  ${}^2A_{2u} \leftarrow {}^2E_{1g}$  transition is probably red shifted  $\sim 700\text{ cm}^{-1}$ , based on the absorption for toluene ion,<sup>36</sup> which is larger than the shift<sup>6</sup> for  $C_6F_6^+$ . The hole in the  ${}^2E_{2g}(\sigma)$  state is somewhat screened from the matrix by aromatic  $\pi$  electrons, which is likely to result in a weaker matrix interaction for the excited  $\sigma$  state than the ground  $\pi$  state. This difference can produce a substantial blue shift for the forbidden  ${}^2E_{2g} \leftarrow {}^2E_{1g}$  transition and cause the  ${}^2A_{2u}$  state to be lower in solid argon, as is the case for  $C_6F_6^+$ . Accordingly, the  ${}^2A_{2u} \leftarrow {}^2E_{1g}$  absorption and emission<sup>45</sup> spectra for benzene cation in solid argon can be explained without complication from the  ${}^2E_{2g}$  state. This, of course, requires that the sharp, weak 552.5 nm band be assigned to an unidentified photosensitive species.

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