origins with thresholds about 100 cm^{-1} above the band peaks. The matrix absorptions for PFT$^+$ and OFT$^+$ are sufficiently sharp to determine which isomer is present. Although the gas-phase PDS peaks for these isomers show PFT$^+$ at 0.04 eV higher energy than OFT$^+$, the large bandwidths prevent as accurate a determination of the PDS band peak as can be made in the solid argon matrix. Similar bandwidth observations have been noted for toluene cation although the differences were not quite as pronounced.[12]

A major affect of the solid argon matrix is to quench internal energy from the parent ions in the condensing layer after photoionization. The presence of excess internal energy may account, in part, for the greater width of the PDS bands. Finally, and of most interest, quenching of internal energy by the matrix allows rearrangement to compete with dissociation, particularly in the case of chlorotoluenes where gas-phase work gives dissociation before rearrangement.[5] A similar enhancement of rearrangement has been found in recent toluene–cycloheptatriene matrix studies.[12]

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Visible Absorption Spectra and Two-Photon Photodissociation of Halobenzene Cations in Solid Argon

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Abstract: Matrix photoionization experiments with bromobenzene, chlorobenzene, and fluorobenzene precursors produced absorptions due to bromobenzene cation at 505 ± 5 nm, chlorobenzene cation at 470 ± 2 nm, and fluorobenzene cation at 431 ± 1 nm, respectively, in excellent agreement with gas-phase photodissociation and photoelectron spectra. Two-photon dissociation of the bromobenzene and chlorobenzene cations in solid argon was affected by photolysis in the very strong visible $n_z \rightarrow \pi$ charge-transfer electronic transition, as found in earlier gas-phase work. The lack of significant two-photon dissociation of fluorobenzene cation is attributed to lower oscillator strength for the $\pi \rightarrow \pi$ transition corresponding to absorption of the first photon.

Introduction

Gas-phase studies of molecular ions by photoelectron and photodissociation spectroscopies (PES and PDS, respectively) are nicely complimented by visible–ultraviolet absorption spectroscopy of the transients isolated in inert gas matrices at cryogenic temperatures, as demonstrated by very recent matrix-isolation work with substituted aromatic precursors. A matrix photoionization study of several halotoluene isomers[1] gave absorptions in very good agreement with previous gas-phase work[2] and provided new evidence for parent cation rearrangement. Toluene and cycloheptatriene cations have been observed in solid argon,[3,4] in very good agreement with the gas-phase data;[5,6] cycloheptatriene cation was isomerized to toluene cation in the matrix environment with visible photolysis.[4] This unique result, in conjunction with evidence for the reverse rearrangement in the gas phase,[7] lends strong support to the postulated equilibrium between the two isomeric cations at low internal energies.[8,9]

One particularly interesting photochemical phenomenon involving aromatic precursors, studied recently in the gas phase, is the two-photon dissociation of benzene, cyanobenzene, and halobenzene cations.[10–13] The purpose of this study is to compare gas-phase and matrix observations of the halobenzene cations and examine their photochemistry in a matrix environment.

Experimental Section

The cryogenic apparatus and windowless argon resonance lamp have been described previously.[14,15] Samples of fluorobenzene (Aldrich), chlorobenzene, and bromobenzene (both Baker) and C_6D_5Br (Aldrich) were outgassed and vacuum-distilled from glass beads and then used undiluted or diluted to M/R (matrix/reactant) = 100/1 or 200/1 concentrations. Samples were condensed through a needle valve at about 1 mM/h for several hours on a sapphire window at 20 K. Simultaneous deposition of argon from the 3-mm i.d. orifice discharge tube caused the final matrix concentrations to be approximately half that of the original sample. Spectra were taken on a Cary 17 spectrophotometer from 800 nm to parent absorptions near 270 nm. Each compound was deposited without discharge radiation to determine precursor absorptions. Photolyses were performed with a high-pressure mercury arc (1000-W, BH-6-1, Illumination Industries, Inc.) using an ultraviolet mirror and Corning glass short-wavelength cutoff filters; high-resolution spectra were recorded at 0.2 nm/s and 6 nm/in. before and after each photolysis.

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(1) Keelan, B. W.; Andrews, L. *J. Am. Chem. Soc.* **1981**, *103*, 99.

(2) Fu, E. W.; Dymerski, P. P.; Dunbar, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 337.

(3) Andrews, L.; Miller, J. H.; Keelan, B. W. *Chem. Phys. Lett.* **1980**, *71*, 207.

(4) Andrews, L.; Keelan, B. W. *J. Am. Chem. Soc.* **1980**, *102*, 5732.

(5) Dymerski, P. P.; Fu, E.; Dunbar, R. C. *J. Am. Chem. Soc.* **1974**, *96*, 4109.

(6) Dunbar, R. C.; Fu, E. W. *J. Am. Chem. Soc.* **1973**, *95*, 2716.

(7) Jackson, J.-A. A.; Lias, S. G.; Auloos, P. *J. Am. Chem. Soc.* **1977**, *99*, 7515.

(8) McLafferty, F. W.; Winkler, J. *J. Am. Chem. Soc.* **1974**, *96*, 5182.

(9) Dunbar, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 1382.

(10) Freiser, B. S.; Beauchamp, J. L. *Chem. Phys. Lett.* **1975**, *35*, 35.

(11) Orlowski, T. E.; Freiser, B. S.; Beauchamp, J. L. *Chem. Phys.* **1976**, *16*, 439.

(12) Dunbar, R. C.; Fu, E. W. *J. Phys. Chem.* **1977**, *81*, 1531.

(13) Dunbar, R. C.; Teng, H. H-I.; Fu, E. W. *J. Am. Chem. Soc.* **1979**, *101*, 6506.

(14) Andrews, L. *J. Chem. Phys.* **1975**, *63*, 4465.

(15) Andrews, L.; Tevault, D. E.; Samardzewski, R. R. *Appl. Spectrosc.* **1978**, *32*, 157.

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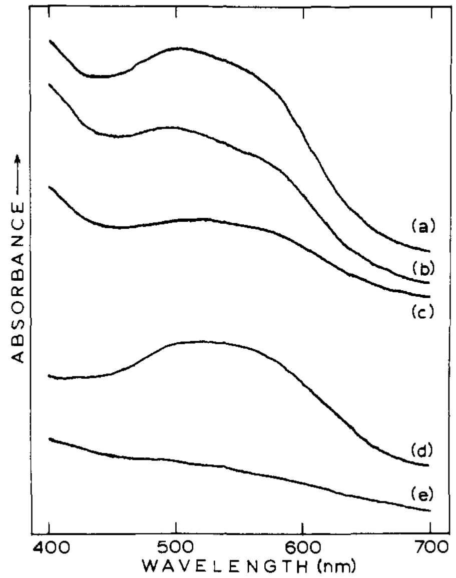


Figure 1. Visible spectra recorded after codepositing bromobenzene vapor with argon from windowless discharge at 20 K: (a) C_6H_5Br codeposited for 4 h; (b) after 15 min 500–1000-nm photolysis; (c) after 15 min 420–1000-nm photolysis; (d) C_6D_5Br codeposited for 3 h; (e) after 30 min 500–1000-nm photolysis.

Results

Bromobenzene. Four experiments were performed with natural isotopic bromobenzene samples, and three were done with fully deuterated bromobenzene samples. The yields of each of the product absorptions were found to depend upon sample concentration.

An Ar/C_6H_5Br = 100/1 sample was codeposited with argon-discharge radiation for 2 h, and the spectrum was recorded from 300 to 1200 nm; strong precursor absorption and sample scattering prevented observation of any product absorption in the 200–300-nm region. The only product was a broad (fwhm = full-width at half-maximum = 120 nm), weak (A = absorbance = 0.04), unstructured absorption centered at 540 ± 5 nm which was reduced substantially upon full arc (220–1000 nm) photolysis and a relatively sharp 278-nm band increased markedly (to A = 0.13). An Ar/C_6D_5Br = 100/1 experiment gave the same broad 540 ± 5-nm band. Photolysis with 420-nm cutoff radiation decreased the short wavelength side of the band leaving a broad 570-nm absorption; full-arc photolysis essentially destroyed the absorption.

Two experiments were performed with undiluted C_6H_5Br equilibrium vapor deposited neat through the needle valve with argon from the open-discharge tube; the C_6H_5Br absorption growth rate was comparable to that of experiments with prediluted bromobenzene. Spectra from one experiment are shown in Figure 1. The 540-nm band (A = 0.12), present in both experiments in greatly enhanced yield over the M/R = 100/1 study, appears to contain unresolved absorptions. Resolving the broad band into two Gaussian bands gives peaks at 505 and 570 nm each with 2600-cm^{-1} full-widths at half-maximum. In one experiment, the 570-nm peak was stronger than the 505-nm maximum; 630-nm photolysis reduced the long-wavelength half of the absorption, giving a band like that shown in Figure 1a. Photolysis with 500-nm cutoff radiation halved the band (to A = 0.06), and the spectrum in Figure 1b again suggests the presence of two maxima near 505 and 570 nm. Photolysis with 420-nm light further decreased the absorption (to A = 0.04), as shown in Figure 1c. Additional photolyses had no effect on the absorption. An undiluted C_6D_5Br experiment also produced the 540-nm band in high yield (A = 0.09); 500-nm photolysis of this particularly transparent sample virtually destroyed the absorption as shown in Figure 1d,e.

In contrast to the undiluted and M/R = 100/1 experiments, no broad 540-nm absorption was observed in two M/R = 200/1 studies. In the natural isotope experiment, a six-member progression was seen at 573.8, 565.7, 558.2, 550.7, 543.5, and 536.3 nm with a mean spacing of 244 ± 5 cm^{-1} and a Franck–Condon maximum at 558.2 nm (A = 0.008). The progression resisted 290-nm photolysis but was approximately halved in intensity by 220-nm photolysis. The deuterium experiment gave a greater product yield. A five-member progression at 581.2, 572.8, 565.0, 557.0, and 549.6 nm possessed a mean spacing of 247 ± 5 cm^{-1} and a Franck–Condon maximum at 557.0 nm (A = 0.009), consistent with its identification as the deuterium analogue of the natural isotope progression. The deuterated species resisted even 220-nm photolysis.

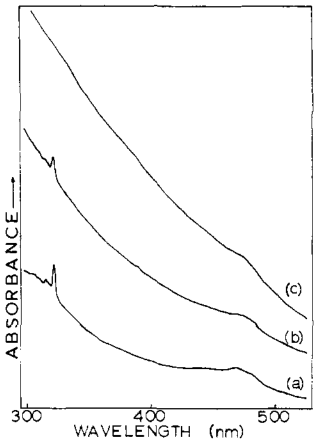


Figure 2. Absorption spectrum recorded after codepositing chlorobenzene sample with argon from windowless discharge at 20 K: (a) Ar/C_6H_5Cl = 100/1 codepostied for 4 h; (b) after 30 min 420–1000-nm photolysis; (c) after 30 min 290–1000-nm photolysis.

Chlorobenzene. Six chlorobenzene experiments were done with Ar/C_6H_5Cl = 100/1 and 200/1 samples. In the Ar/C_6H_5Cl = 100/1 experiments, photoionization of the precursor during condensation produced a broad band with two maxima at 470 ± 2 nm (A = 0.040) and 482 ± 2 nm (A = 0.030) shown in Figure 2a. A new band was observed at 322.0 nm (A = 0.08) with associated structure at 318, 315, 310, and 306 nm. Photolysis with 420–1000-nm radiation for 30 min reduced the 470- and 482-nm bands (to A = 0.020) and the 322-nm system (to A = 0.05) (Figure 2b). Subsequent 290-nm photolysis destroyed the 322-nm absorption but did not affect the 470- and 482-nm bands (Figure 2c). In other experiments, the broad 470-nm band was destroyed upon full-arc photolysis, and weak 402- and 410-nm bands (A = 0.005) were observed to increase on visible photolysis.

Fluorobenzene. Three experiments were performed with fluorobenzene. Deposition of equilibrium C_6H_5F vapor at −24 °C through the needle valve with argon from the open discharge gave a growth of precursor absorption comparable to the following diluted sample experiment; the only product was a band at 430 nm (A = 0.010) which was decreased slightly by 380-nm photolysis (to A = 0.09) but was destroyed by 220-nm radiation (Figure 3a–c). Another experiment using an Ar/C_6H_5F = 100/1 sample gave a broad 430-nm band (A = 0.008) and bands at 325 nm (A = 0.008), 317 nm (A = 0.012), and 310 nm (A = 0.028). Photolysis with 290-nm radiation for 30 min did not alter the 325-nm band, approximately halved the 430- and 317-nm bands, and reduced the 310-nm band (to A = 0.022). Full-arc photolysis destroyed the former three bands and reduced the latter absorption (to A = 0.018). An Ar/C_6H_5F = 200/1 experiment yielded only a four-member progression at 552.2, 547.8, 540.8, and 534.4 nm, with a mean spacing at 233 cm^{-1} and maximum at 540.8 (A = 0.024), which was completely destroyed upon 220-nm photolysis.

For comparison, a toluene experiment was performed, codepositing toluene vapor (−24 °C equilibrium) with argon from the open discharge; the major product was the toluene cation absorption at 430 nm (A = 0.011); in addition the cycloheptatriene cation was observed at 480 nm (A = 0.001) and the benzyl radical absorption was found at 310 nm (A = 0.02), reported in the previous argon/toluene = 100/1 experiments.[3] Photolysis with 420-nm radiation virtually destroyed the 430-nm absorption

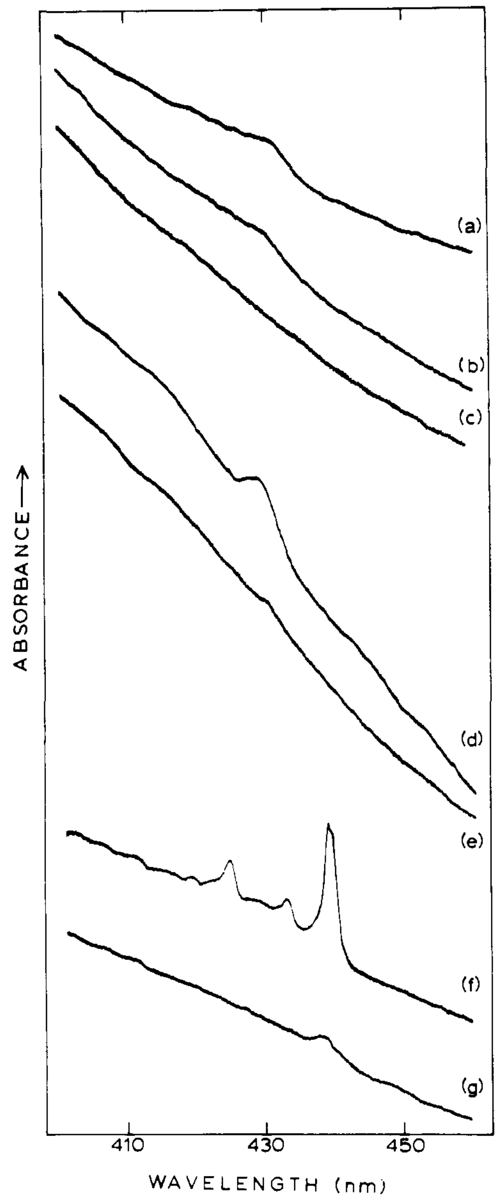


Figure 3. Visible spectra recorded after codepositing fluoro- and methyl-substituted benzenes with argon from windowless discharge at 20 K: (a) C_6H_5F vapor at -24 °C codeposited for 3 h; (b) after 15 min 380–1000-nm photolysis; (c) after 15 min 220–1000-nm photolysis; (d) $C_6H_5CH_3$ vapor at -24 °C codeposited for 90 min; (e) 30 min photolysis with 350–470-nm filter; (f) Ar/p-$FC_6H_4CH_3$ = 200/1 codeposited for 3 h; (g) after 15 min 420–1000-nm photolysis.

(Figure 3 d–e). Figure 3f–g also shows a p-fluorotoluene study using a 1% sample in argon; the strong 438-nm origin and vibrational structure at 432 and 424 nm were virtually destroyed by 420-nm photolysis.[1]

Discussion

The new product absorptions will be identified and compared to gas-phase spectra.

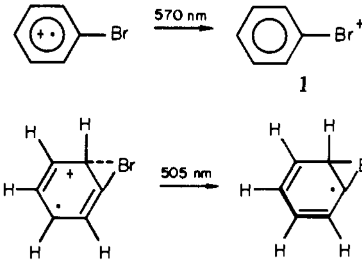
Identification. Bromobenzene cation photodissociation has been observed in ion cyclotron resonance studies below the one-photon energetic threshold; a sequential two-photon photodissociation process peaking at 2.55 or 2.45 eV[12,13] (hereafter 2.50 ± 0.05 eV) has been supported by a kinetic analysis.[12] Similar work on chlorobenzene cation yielded a peak in the two-photon dissociation region at 2.70 ± 0.05 eV, and although some dissociation of fluorobenzene ion was observed near 3 eV, no photodissociation spectrum could be obtained.[13]

The short-wavelength maximum at 505 nm in bromobenzene matrix experiments is slightly red-shifted from the 2.50 ± 0.05 eV (490 ± 10 nm) gas-phase PDS maximum; the matrix band position and its photodissociation with 500-nm radiation support assignment of the 505-nm absorption to bromobenzene cation. The 470-nm short-wavelength maximum in similar chlorobenzene studies is also slightly red-shifted from the 2.70-eV (459 nm) PDS maximum, and it photolyzes substantially with 420-nm radiation, which suggest assignment to the chlorobenzene cation. Unfortunately, the ultraviolet absorption of these halobenzene cations, observed at 4.0–4.4 eV by PDS methods,[13] could not be observed here due to strong neutral precursor absorption.

The 430-nm absorption in fluorobenzene experiments is just lower in energy than the 2.95-eV (420 nm) difference between the onset of ionization and the Franck-Condon maximum in the PES of fluorobenzene[16] and the weak absorption reported near 427 nm in neon matrix photoionization experiments.[17] It is noteworthy that the 430-nm argon matrix band, assigned to fluorobenzene cation, decreased about 10% on 380-nm photolysis and was essentially destroyed by full-arc photolysis.

It is proposed that the halobenzene cations are formed by photoionization with 11.6–11.8-eV argon resonance radiation from the open discharge[15] which is in excess of the 9.1 ± 0.1-eV ionization energies of the halobenzenes[16] and that the ions are trapped in the condensing matrix.

The chlorobenzene and bromobenzene ion absorptions exhibited two maxima in the argon matrix experiments. The shorter wavelength peak, described above, is in excellent agreement with the PDS peaks for the respective cations. The longer wavelength peak is approximately 500 cm^{-1} lower for chlorobenzene and 2300 cm^{-1} lower for bromobenzene. The relevant PES band for bromobenzene at 2.20 eV above adiabatic ionization is in very good agreement with the longer wavelength matrix peak. The PDS-PES difference for bromobenzene cation suggests an ion geometry change with consequently different Franck–Condon band envelopes, as proposed earlier.[13] The observation of two matrix peaks, one in agreement with the PDS band position and the other in agreement with the PES band difference above ionization, suggests that two different structures for the parent cation are trapped in the matrix. The longer wavelength maximum for bromobenzene cation, in agreement with the PES band difference, is assigned to the cation with the structure of the ground state molecule, **1**. The shorter wavelength maximum for bromobenzene cation, in agreement with the PDS peak, is attributed to the cation with a slightly different structure, which is suggested to involve the halonium species, **2**. The two peaks in the bromobenzene experiments were selectively decreased by photolysis on the long- or short-wavelength sides of the band, which suggests that two different structures contribute to the spectrum. Likewise, the 470-nm chlorobenzene cation peak is reduced more than the 482-nm peak on 420-nm photolysis, in support of this hypothesis.



A comparison of band width between PDS and matrix absorption spectra is of interest. Matrix studies of toluene cation revealed an order of magnitude sharper band than observed in PDS,[5] which was attributed largely to quenching of internal energy by the matrix.[4] Comparison in the chlorobenzene and bromobenzene cases is complicated by two apparent excited-state

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(16) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. "Molecular Photoelectron Spectroscopy"; Wiley-Interscience: New York, 1970.

(17) Bondybey, V. E.; Miller, T. A.; English, J. H. *J. Chem. Phys.* **1980**, *72*, 2193.

(18) Dill, J. D.; Schleyer, P. V. R.; Binkley, J. S.; Seeger, R.; Pople, J. A.; Haselbach, E. *J. Am. Chem. Soc.* **1976**, *98*, 5428.

structures, but approximate measures of the two deconvoluted bandwidths give about 600 cm^{-1} for chlorobenzene cation and 2600 cm^{-1} for bromobenzene cation. The PDS bandwidths for chlorobenzene and bromobenzene cations are about 3500 and 5800 cm^{-1}, respectively.[13] The matrix bands are clearly sharper than the PDS bands, but the difference is not as pronounced as in the case of toluene cation.

Photolysis of chlorobenzene and bromobenzene cations in ICR work gave a halogen atom and phenyl cation.[13] The major change on photolysis in these experiments was the growth of a relatively sharp 278-nm band with destruction of the broad 505- and 570-nm peaks in bromobenzene experiments. Although no spectroscopic data is available for phenyl cation, recent STO-3G calculations have predicted the ground state to be a singlet with an enlarged C–C$^+$–C angle. This cation could reasonably be expected to absorb near the similar π system of benzene in the 200-nm region. The 278-nm absorption might be due to phenyl cation; however, there is insufficient evidence for a definitive identification.

The 0–0 bands of the three fluorophenyl radicals have been observed in the gas phase at 623 nm (ortho), 574 nm (para), and 544 nm (meta); *p*-bromophenyl and *m*-bromophenyl have been seen at 539 and 540 nm, respectively.[19] The vibrational progression in the fluorobenzene experiment commencing at 555.2 nm is appropriate for the *m*-fluorophenyl free radical, assuming the usual small matrix red-shift. As hydrogen detachment is energetically favored over fluorine detachment, it is reasonable for this radical to be formed; however, the absence of the two other isomers is not easily explained. It is conceivable that the progression in the C_6H_5Br experiment, starting at 573.8 nm and having a 247 ± 5-cm^{-1} averaged spacing, is one of the bromophenyl radicals; the 1-nm blue deuterium shift in the C_6D_5Br experiment is consistent with this identification.

The 322-nm band observed in chlorobenzene experiments and the 317-nm band found in fluorobenzene studies may be due to halocyclohexadienyl radicals, formed by addition of a hydrogen atom to the parent molecule. Cyclohexadienyl radical, made from the benzene precursor, absorbed at 310 nm in solid argon,[20] and methylcyclohexadienyl radical, produced from toluene, were observed at 317 nm in solid argon.[5] The present 322- and 317-nm bands exhibit similar photochemistry as cyclohexadienyl radical in solid argon. The weak 402- and 410-nm absorptions in chlorobenzene studies and 310- and 325-nm bands in fluorobenzene work cannot be identified.

Two-Photon Dissociation. Two-photon dissociation of the heavy halobenzene cations with visible light has been documented in the gas phase.[12,13] This process involves absorption by the first photon into the excited state, followed by internal conversion to high vibrational levels of the ground electronic state and absorption of a second photon into dissociation. In the present matrix experiments, bromobenzene cation was markedly reduced by 500-nm photolysis, which is below the 355 ± 5-nm one-photon dissociation threshold for bromine atom elimination, and chlorobenzene cation was substantially reduced by 420-nm photolysis, below the 310 ± 5-nm one-photon threshold for chlorine atom detachment.[13,21] This shows that sequential two-photon processes can take place in a solid argon matrix when the oscillator strength of the transition is large enough to produce absorption by chlorobenzene and bromobenzene cations before most of their internal energy is removed by the matrix host. A similar two-photon dissociation of styrene cation has been observed in solid argon.[22] Antistokes emission of Ca_2 in solid krypton has been also rationalized by a similar two-photon absorption scheme.[23]

In contrast, the fluorobenzene cation was not significantly decreased upon 380-nm photolysis, though it was destroyed with 220 nm radiation, which is above the one-photon threshold. This may be rationalized by the fact that the $n_z \rightarrow \pi$ charge-transfer transitions in chlorobenzene and bromobenzene cations have very high oscillator strengths, but due to the small interaction of the fluorine lone pair electrons with the ring π electrons, the visible transition for fluorobenzene is $\pi \rightarrow \pi$, which has a lower oscillator strength.

Although the matrix effectively quenches internal energy from the absorbing species, sequential two-photon processes are possible in a matrix environment when the cross section for initial photon absorption is particularly large. The fact that quenching of internal energy from a polyatomic cation in a solid argon matrix requires a finite amount of time is verified by the observation of isomerization of cycloheptatriene cation to toluene cation upon absorption by the former cation above the threshold for dissociation.[4] With continuous pumping of internal energy through an electronic absorption, cycloheptatriene cation retains sufficient internal energy for isomerization in the solid argon environment.

The matrix cage also has a static as well as a dynamic effect on dissociation. The well-known "cage effect" prohibits large photodissociation products from separating after bond rupture; this effect will be more pronounced for Br > Cl > HF, which are the dissociation products[13] of the halobenzene cation studied here. Recombination of $C_6H_5^+$ and Br or Cl in the matrix cage clearly reduces the dissociation observed in the matrix. The matrix cage, however, does not affect the general trend observed here, namely, that bromobenzene cation photodissociates more readily than chlorobenzene and fluorobenzene cations in that order.

Substituent Effects. In general, alkyl substituents on a benzene ring are expected to have little affect on the electronic transitions of the π electrons in the ring due to minimal ring-substituent orbital interaction. Theoretical considerations also indicate that the tightly bound fluorine lone-pair electrons interact negligibly with ring π electrons.[24,25] Hence, the spectra of all of the fluoro- and methyl-substituted benzene cations are expected to be similar. This is dramatically shown in Figure 3; fluorobenzene cation at 431 nm, *p*-fluorotoluene cation at 438 nm, and toluene cation at 430 nm are nicely clustered, as predicted by theory and observed in PDS experiments.[2,13]

Conclusions

Absorption spectra of bromobenzene and chlorobenzene cations in solid argon are in excellent agreement with gas-phase PDS and PES data, and the spectrum of fluorobenzene cation in argon is virtually identical with that obtained previously in neon. Evidence is presented for two different structures for chlorobenzene and bromobenzene cations. As in the gas phase, two-photon dissociation with visible photons was observed in the matrix for bromobenzene and chlorobenzene cations in the very strong $n_z \rightarrow \pi$ charge-transfer band but not with fluorobenzene Two-photon dissociation processes in the matrix require a very large cross section for the initial photon absorption in order to overcome the rapid quenching of internal energy by the matrix. The insensitivity of aromatic $\pi \rightarrow \pi$ transitions to fluoro and methyl substituents, illustrated by comparison of the spectra of fluorobenzene, fluorotoluene, and toluene cations in solid argon, attests to the lack of interaction of these substituents with the aromatic ring.

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[19] Porter, G.; Ward, B. *Proc. R. Soc. London, Ser. A* **1965**, *287A*, 457.

[20] Miller, J. H.; Andrews, L.; Lund, P. A.; Schatz, P. N. *J. Chem. Phys.* **1980**, *73*, 4932.

[21] Photobleaching of trapped halide ions can provide electrons to neutralize trapped cations, as has been discussed previously (Prochaska, F. T.; Andrews, L. *J. Am. Chem. Soc.* **1978**, *100*, 2102). However, the 420- and 500-nm radiation used here to photolyze chlorobenzene and bromobenzene cations, respectively, has insufficent energy to photodetach electrons from chloride and bromide ions.

[22] Andrews, L.; Harvey, J. A.; Kelsall, B. J.; Duffey, D. C., to be submitted for publication.

[23] Miller, J. C.; Andrews, L. *J. Chem. Phys.* **1978**, *68*, 1701.

[24] Marshner, F. *Tetrahedron* **1975**, *31*, 2303.

[25] Debies, T. P.; Rabalais, J. W. *J. Electron Spectrosc. Relat. Phenom.* **1972**, *1*, 355.