xenon arc lamp.

All of the samples with the exception of the ferrocene and ferricenium tetrafluoroborate were loaded into the cell in a drybox under N_2. The sample and microphone chambers were flushed with at least 20 times their volumes of dry N_2. All of the spectra were corrected for the nonidealities of the optical system by dividing the spectra by a carbon black reference. The resolution for the ferricenium salt spectrum is 16 nm. All of the other spectra have a resolution of 8 nm. The pure powder spectra were taken at a modulation frequency of 400 Hz in order to avoid signal saturation. The ferricenium salt was run at 2 kHz to reduce saturation effects due to the strong absorption of this pure sample. The samples on the silica were run at 80 Hz.

Acknowledgments. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences (Contract EG-77-S-02-4178.A002 to M.S.W.), the National Science Foundation (Grant DMR-76-80895 to R.H.S.), and the Joint Services Electronics Program (Contract DAAB07-76-C-1400 to R.H.S.). M.S.W. acknowledges support as a Dreyfus Teacher–Scholar grant recipient, 1975–1980.

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Photodissociation Spectroscopy of Halogen-Substituted Benzene Ions

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Received March 22, 1979

Abstract: Photodissociation spectra of the four halobenzene gas-phase parent ions are presented, obtained by a combination of one-photon and two-photon photodissociation. The spectra are compared with the corresponding halotoluene ion spectra, with the photoelectron spectra of neutrals, and with theory. The close similarity of halobenzene and halotoluene spectra indicates a minor perturbing role for the methyl group. It is concluded from the analysis that the fluorine substituent has little or no spectroscopic manifestation but that, in the other halobenzene ions, the halogen substituent plays an important spectroscopic role, in particular contributing a prominent spectral feature having halogen-to-ring charge transfer character. Comparison of peak positions in the photodissociation and photoelectron spectra in the bromobenzene and iodobenzene cases suggests that the ion ground state is substantially distorted relative to the neutral molecule.

Introduction

The photodissociation spectrum of a gas-phase ion is the wavelength dependence of the rate of photodecomposition of the ion. As has been shown in numerous cases,[1d] such a spectrum is a valuable source of information about the position of optical absorption features for the ion, and, since direct optical absorption spectra of most gas-phase ions are currently not obtainable, photodissociation spectra have been interpreted and used for their optical spectroscopic value.

It is thus beginning to be possible to map out systematically the spectroscopy of gas-phase cations, and, just as with neutral-molecule spectroscopy, the aromatics constitute an exceptionally interesting group among larger polyatomics. The spectroscopy of benzene cation and its methyl derivatives has moved some distance toward a satisfactory understanding,[2] but less attention has gone to developing systematic understanding of resonance-interacting substituents on benzene cation. For the halogen substituents treated here, the substituent plays an important role in determining the qualitative features of the spectroscopy, in contrast to the neutral molecules in which the spectroscopic role of the halogen is hardly observable. We believe that a coherent interpretation of the halobenzene ion spectra is now feasible.

Spectra of a number of halotoluene ions were reported some time ago,[3,4] but there are several drawbacks to basing an analysis on these alone: the possible effect of the methyl substituent is unknown; the π and σ electronic systems are not fully separated so that calculations are not convenient; and the photoelectron spectra of these molecules do not show the sharp peaks needed for quantitative comparisons.

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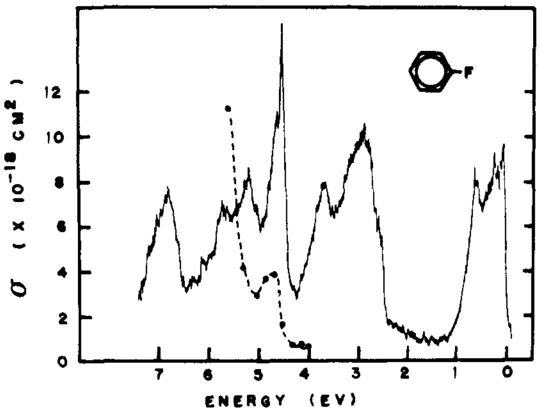

Figure 1. Photodissociation spectrum (dashed line with data points) and photoelectron spectrum (light solid line) of fluorobenzene cation and neutral, respectively. The PES energy scale is shifted to put the first IP at zero.

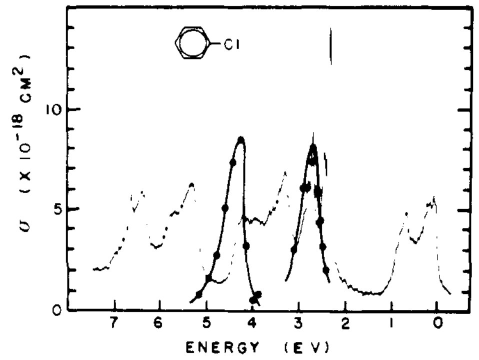

Figure 2. Spectra for chlorobenzene. The absolute cross-section scale refers only to the UV peak, the visible peak being uncalibrated.

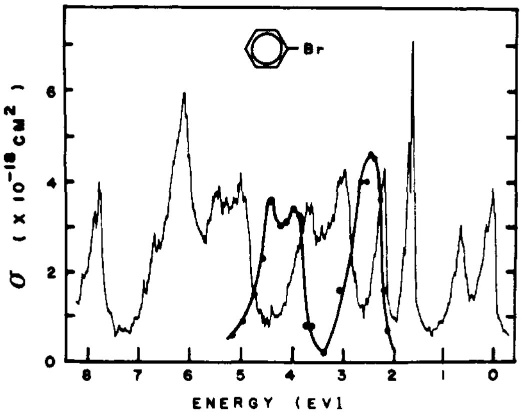

Figure 3. Spectra for bromobenzene.

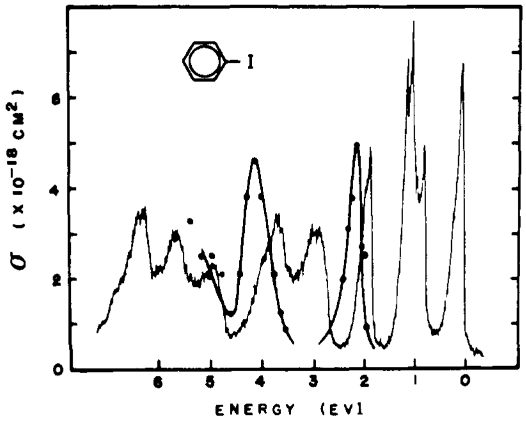

Figure 4. Spectra for iodobenzene. The cross-section scale refers only to the UV peak, the visible peak being uncalibrated.

The halobenzene ions are satisfactory subjects for study in all of these respects, but had been considered inaccessible to photodissociation studies because one-photon dissociation in the visible wavelength region is energetically impossible. However, the development of two-photon photodissociation spectroscopy has changed this,[5,6] and we report and discuss here one- and two-photon spectra of the halobenzene ions. Excellent photoelectron spectra are available for the halobenzenes.[7] Also useful in the interpretation are the PPP-CI calculations of Marschner indicating the nature of the occupied orbitals,[8] and the PES spectra and INDO and CNDO/2 calculations of Debies and Rabalais.[9] For the purpose of estimating transition moments, we have also supplemented these calculations with some MINDO/3 all-electron calculations.

Experimental Section

The techniques of obtaining photodissociation spectra by using the ICR spectrometer have been described.[3,4] The UV portions of the spectra were all obtained with a 2.5-kW Hg–Xe arc lamp at 14-nm monochromator resolution. In the visible region, arc-lamp spectra were obtained for chlorobenzene, bromobenzene, and iodobenzene ions; some points on the chlorobenzene and bromobenzene ion spectra were obtained with lines from a Coherent Radiation CR-12 argon-ion laser; and some points on the iodobenzene ion spectrum were obtained with the Coherent Radiation Model 490 argon-ion-pumped dye laser.

Spectra of all the ions were obtained in the steady-state ICR mode of operation. Portions of the spectra were rechecked with our more recent pulsed-ICR system; a few points of modest discrepancy were resolved putting more weight on the more recent, intrinsically more reliable pulsed-ICR data, particularly in assigning absolute cross sections.

For transition moment calculations, a standard MINDO/3 program was modified to compute the transition moment from the radical-ion ground state to the excited hole state, using expressions from ref 10.

Results

Photodissociation spectra for the four halobenzene ions are shown in Figures 1-4, with the PES spectra superimposed. (For comparison, spectra of the halotoluenes are given in ref 3.) For fluorobenzene ion, the points were all treated as one-photon dissociations for the cross-section calculation. In addition, a peak is expected for fluorobenzene near 3 eV, and some photodissociation was observed at 400 nm, but no meaningful cross-section measurement or spectrum could be obtained. For the other molecules, the UV peaks are treated as one-photon transitions and the cross-section values are one-photon cross sections.

The two-photon spectrum of bromobenzene ion at visible wavelengths was the object of a careful previous study,[6b] and the very well behaved data probably give a reliable set of cross sections for effective one-photon absorption. Accordingly, the cross sections in the visible region of Figure 3 are the calculated one-photon equivalent values from this two-photon analysis.

The chlorobenzene spectrum in the two-photon (visible) wavelength region was treated by using the approximate data reduction procedure previously described.[6b] The arc-lamp points from 400 to 480 nm were scaled to overlap smoothly the argon-ion laser points from 458 to 515 nm, giving what should be a good relative spectrum, but absolute cross sections in the two-photon region were not obtained. The photodissociation rate at 496.5 nm showed good I^2 dependence up to about 0.2-W power, and then leveled off as expected from the two-photon kinetic model.

Iodobenzene ion is notable in having such an extremely in-

Table I

	thermochemical (one-photon) threshold, eV[a]	visible peak		UV peak	
		photodissoc max	PES max	photodissoc max	PES max
$C_6H_5CH_3^+$	2.1	3.0	*c*	4.7	*c*
$C_6H_5F^+$	4.4	*b*	*c*	(4.7)	4.6
p-$C_7H_7F^+$	2.4	3.0	*c*	4.5	4.5
$C_6H_5Cl^+$	4.0	2.7	2.75	4.25	4.15[d]
p-$C_7H_7Cl^+$	1.8	2.7	2.7	4.25	4.2[d]
$C_6H_5Br^+$	3.5	2.45	2.20	4.0, 4.4	3.8[d]
p-$C_7H_7Br^+$	1.2	2.50	2.3	4.05	3.8[d]
$C_6H_5I^+$	3.1	2.15	1.90	4.15	3.60[d]
p-$C_7H_7I^+$	0.8	2.15	1.9	3.95	3.7[d]

[a] Energetics from ref 11. [b] Some photodissociation observed at 400 nm; but no spectrum was obtained. [c] Peak assignments not known. [d] These assignments are more or less speculative. See text and ref 8 for discussion.

tense two-photon spectrum in the visible region that it was possible to obtain the entire spectrum with the arc-lamp source. The iodobenzene two-photon data were not well behaved, in that they did not give good I^2 intensity dependence. This may be a case where the low-intensity, high-pressure approximations break down at relatively low intensity levels, and there were also indications of unresolved difficulties with parent-ion regeneration from photoproducts; it did not seem that quantitative two-photon cross-section analysis of the data would be reliable, so that this spectrum, also, is reported only as a relative spectrum.

"Time-resolved", or exhaustive photodissociation,[4] studies were made of the ions and indicated that the ion populations were spectroscopically homogeneous. There was no indication of nondissociative components, or of a variation in cross section for different ions in the population.

Chlorobenzene, bromobenzene, and iodobenzene ions dissociate as expected to the most stable set of products, $C_6H_5^+$ + (halogen atom), and no other products were observed. The expected product for fluorobenzene ion is $C_6H_4^+$ + HF, but this was not experimentally confirmed. The thermochemistry of the ions based on these dissociation channels is indicated in Table I.

Discussion

Fluorobenzene. The spectrum obtained for fluorobenzene is not very informative, since the thermochemical threshold lies so high as to make it likely that thermochemical effects dominate the photodissociation spectrum below 4.5 eV. The fluorotoluene ion spectrum is a much better basis for spectral interpretation. Figure 5 shows an interpretation such as we wish to make for all of the spectra, in terms of interaction between the benzene-ring π orbitals and the lone-pair orbitals of the halogen. Orbitals are plotted on the energy scale according to their binding energy, the highest occupied orbital being that plotted at lowest binding energy. The orbital energies are estimated from photoelectron results[7,9] and from calculations.[8,9] The hole states of the radical ion are derived by putting the electron hole in the appropriate orbital, giving ground and excited electronic states in the usual way.

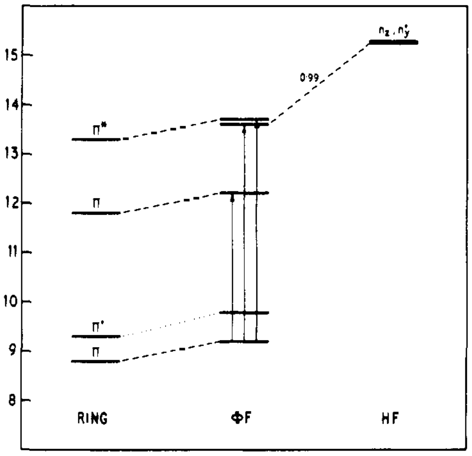

Figure 5. Orbital interaction diagram for fluorobenzene, showing the interaction of benzene-ring and fluorine lone-pair orbitals. The binding energies (eV) for the orbitals are taken where possible from PES spectra, and otherwise from theory and/or from the present results. The figure (0.99) on the dashed line leading from n_z (HF) is the estimate from ref 9 of the fractional contribution of the halogen p_z atomic orbital to the fluorobenzene molecular orbital. As discussed in the text, the π* level does not represent an orbital energy, but represents the π* excited state, and has been placed on the diagram at an appropriate excitation energy above the ground state for the purpose of comparison with the hole-promotion excitations. The $\pi \rightarrow n_z$ and $\pi \rightarrow \pi$ arrows denote symmetry-allowed hole-promotion type spectral transitions, while the $\pi \rightarrow \pi^*$ arrow denotes the allowed electron-promotion spectral transition.

Note, however, that the level labeled π* in Figures 5–8 does not properly belong at this position on the orbital diagrams, where it has been placed for convenient comparison. The π* designation represents the excited state (not orbital) of the ion obtained by electron promotion from the highest occupied π orbital to the empty π* orbital. The arrow denoting the $\pi \rightarrow \pi^*$ transition is thus an electron promotion, while the arrows denoting $\pi \rightarrow \pi$ and $\pi \rightarrow$ n transitions are hole promotions. The "RING" states on the left are the (adiabatic) excited π and π* states of toluene ion, which should be a good model system,[2] while the "HF" states on the right are the (degenerate) lone pair (n) orbitals of HF. (The hydrogen halides are chosen as model halogen systems which will model much of the inductive effect, but none of the orbital-interaction effect, for the lone-pair orbitals of the benzene-bound halogen atom.) The principal point of reference in discussing photodissociation spectra of substituted benzene ions is the toluene spectrum, which reflects the $\pi \rightarrow \pi$ transition (3 eV) and the $\pi \rightarrow \pi^*$ transition (4.6 eV) involving the "RING" orbitals at the left-hand side of the figure.

The orbital interaction picture for fluorobenzene ion is particularly simple: there is little effect on the ring orbitals other than a uniform inductive shift, and the fluorine atom simply adds an additional orbital near the position of the ring $\pi \rightarrow \pi^*$ excitation. The figure 0.99 on the interaction line for this orbital gives Marschner's estimate[8] of the fractional contribution the fluorine $2p_z$ orbital makes to the corresponding fluorobenzene n_z orbital, and in this case clearly suggests that there is no significant interaction between ring and halogen. A MINDO/3 calculation indicates more mixing, with the n_z orbital having 81% fluorine $2p_z$ character, while the INDO and CNDO/2 calculations reported by Debies and

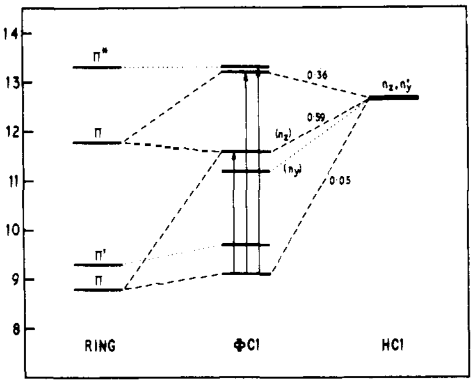

Figure 6. Orbital interaction diagram for chlorobenzene, similar to Figure 5.

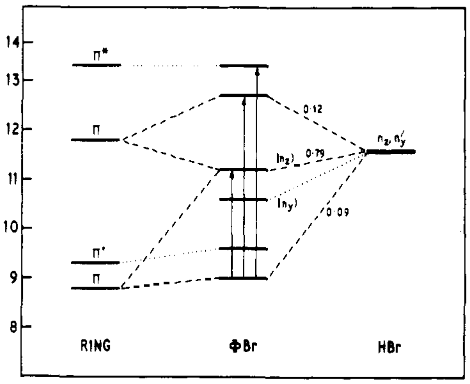

Figure 7. Orbital interaction diagram for bromobenzene, similar to Figure 5.

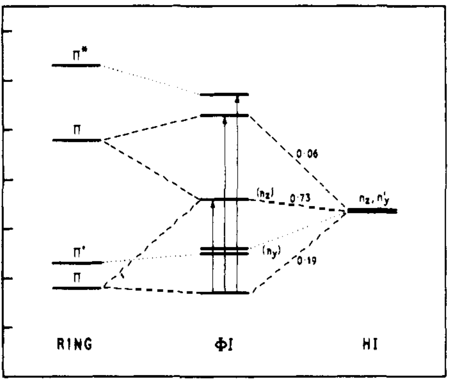

Figure 8. Orbital interaction diagram for iodobenzene, similar to Figure 5.

Rabalais[9] suggest even more mixing, with the fluorine $2p_z$ contribution to n_z being 53%. Thus, while the extent of ring-fluorine interaction is rather uncertain, it seems justifiable to consider the n_z molecular orbital as primarily a fluorine-localized orbital. The MINDO calculation predicts the $\pi \rightarrow \pi$ transition (at 2.9 eV) to be strongly allowed (transition dipole moment 5.5 D), but the $\pi \rightarrow n_z$ ring-to-fluorine charge transfer transition is predicted to be only weakly allowed, with a transition moment of 0.8 D, and might thus be expected to give at most a minor spectral contribution. Thus the expectation from theory is that the fluorobenzene ion spectrum will be very little different from the toluene ion spectrum, the only indicated difference being the possibility of some disturbance of the toluene ion peak near 4.6 eV from the nearby weakly allowed charge transfer transition.

This expectation is nicely borne out in the fluorotoluene ion spectrum, which is essentially indistinguishable from the toluene ion spectrum. For fluorobenzene ion, bearing in mind that two-photon dissociation at energies below the one-photon threshold near 4.4 eV was not sufficiently strongly observed to draw any useful spectroscopic conclusions, the spectrum (Figure 1) is not inconsistent with this picture. It presumably shows the short-wavelength portion of the 4.6 eV peak: the apparent strong rise above 5 eV probably arises from a higher $\pi \rightarrow \pi^*$ transition, of which several are predicted.

The interesting aspect of the fluorobenzene PES spectrum bears on the difficult question of the assignment of the photodissociation feature near 4.6 eV. The PES spectrum shows the n_z orbital to be near this position, so $\pi \rightarrow n_z$ is a possible alternative to the $\pi \rightarrow \pi^*$ assignment favored here. (Note that the π^* orbital corresponds to a double excitation process from the neutral and is thus not expected to give a strong PES peak.) Indications in favor of predominant $\pi \rightarrow \pi^*$ character for this photodissociation peak are the MINDO/3 transition moment result noted above and the fact that in fluorotoluene this peak is similar in absolute intensity to other aromatic $\pi \rightarrow \pi^*$ photodissociation peaks.

Heavy-Halogen Derivatives. Chlorine, bromine, and iodine substituents result in a different situation from fluorine, and, as they give qualitatively similar effects, they may be discussed together. It is noteworthy first that the spectra of halobenzenes (Figures 2-4) are quite similar to those of the corresponding halotoluenes: the peak widths and shapes may differ in detail, but the peak positions are very similar, as shown in Table I. It is clearly justifiable to consider the methyl group as a very small perturbation to the spectroscopic behavior.

The spectra are also superficially similar in pattern to the toluene ion spectrum, and it is at first sight tempting to attempt interpretations based on a slightly perturbed toluene ion. Such attempts fail, and a glance at the PES spectra shows that, in fact, the halogen lone-pair orbitals must play a major spectroscopic role, and that the superficial similarity to the toluene spectrum is misleading. The orbital interaction Figures 6-8 indicate an interpretation consistent with the PES spectra and with calculation. The photodissociation peaks in the visible region correspond to the hole transitions to the halogen lone-pair orbitals. There are two molecular orbitals with halogen lone-pair character, the in-plane (n_y) and the out-of-plane (n_z) orbitals. They are clearly shown as sharp isolated features in the PES spectra, and the higher lying (higher binding energy) of the pair corresponds to an optically allowed transition to n_z from the ion ground state. The $\pi \rightarrow n_y$ transition is symmetry forbidden. The diagrams indicate Marschner's estimate of the extent of halogen p_z atomic orbital contributing to the n_z molecular orbital: for all cases halogen p_z character dominates, and this transition can be characterized as a halogen-to-ring charge transfer process. A MINDO calculation on chlorobenzene indicates that it is strongly allowed (transition dipole moment 6.5 D).

An unexpected feature of these $\pi \rightarrow n_z$ transitions is the lack of exact agreement in peak positions between photodissociation and PES peaks. The discrepancy is worse for the heavier halogens and is most prominent for iodobenzene. There seems no doubt at all that the same excited electronic state of the ion is involved in the two types of spectrum, or that the individual vibronic transitions must necessarily coincide; and there seems little possibility of serious error in the position of the energy zero in the PES spectra since the first PES ionization onsets are very sharp and are in addition very accurately known from optical spectroscopy. Therefore, the peak discrepancy must reflect a difference in the shape of the vibrational peak envelope between the two approaches. Such a difference can be attributed either to differing Franck-Condon factors, or to vibronic discrimination effects.

Differences in Franck-Condon line shape between these two types of spectrum can arise because, while the final state is the same in both cases, the initial state is the neutral molecule for PES, but is the ion ground state for photodissociation. The geometries of three species are important here, namely, the neutral molecule, the ion ground state, and the n_z ion excited state. Of these, the first is known, and the second, the n_z excited state, appears to have similar geometry to the neutral, since for these molecules the PES peaks for the n_z ionizations are very sharp (as expected for removal of a nonbonding electron); however, less is known about the ion ground state geometry, and it is here that the present results are of value. In this interpretation, the blue shift of the photodissociation peak relative to the PES peak reflects directly the distortion of the ion ground state relative to the neutral; some distortion is expected upon removal of the strongly bonding π electron, and these results suggest that this distortion is significant. The highest occupied π orbital has a shape corresponding roughly to an asymmetric ring stretching vibration, and, in the most extreme case of iodobenzene ion, the observed shift corresponds to the excitation of approximately two quanta of such a normal mode. It has been recognized that a comparison of photodissociation and photoelectron spectra provides a possible way of evaluating geometry changes upon ionization, and this case provides an apparent example of such effects.

Alternatively, the photodissociation peak could be shifted to shorter wavelengths if the $v = 0$ and $v = 1$ vibronic states of the n_z excited electronic state have a predominant mode of deexcitation not leading to dissociation: fluorescence would be the logical alternative. We regard this as unlikely because strong fluorescence has not been reported for these ions, and because this would imply a very small peak photodissociation cross section (corresponding to relatively infrequent excitation to the dissociative high vibronic levels), whereas the observed cross sections for bromobenzene and iodotoluene ions are both large, comparable to other intense photodissociation processes. Therefore, it seems most likely that the observed shifts reflect shifts in the optical absorption peaks arising from ion geometry changes and consequent differing Franck-Condon envelopes.

The $\pi \rightarrow \pi$ transition which lies at 3.0 eV in toluene ion is pushed up to near 4 eV by interaction with the halogen lone-pair orbital. The $\pi \rightarrow \pi^*$ excitation is evidently unaffected or slightly lowered by the presence of halogen, and these two transitions thus lie close in energy. Only for bromobenzene is there clear evidence of a split UV peak which could reflect comparable, resolved contributions from both transitions; for the other ions, the UV peak, while more or less broad, is not observably split. The MINDO calculation on chlorobenzene suggests further that the strong interaction of the 11.8-eV π orbital with the halogen substantially reduces the transition moment for the $\pi \rightarrow \pi$ transition, so that, while this transition has a calculated moment of 5 D for toluene ion, it is only 1.1 D for chlorobenzene ion. This suggests that the $\pi \rightarrow \pi$ transition, in addition to being shifted to the vicinity of the $\pi \rightarrow \pi^*$ transition, may also be greatly reduced in intensity. The PES spectra show a peak near 4 eV which is probably the upper π orbital, and whose position is consistent with assigning the $\pi \rightarrow \pi$ optical transition as the long-wavelength portion of the unresolved UV spectral feature. (As already noted, the $\pi \rightarrow \pi^*$ excited state, as a double excitation ionization from the neutral, is not expected to give a strong PES peak.)

An assumption in all of the analyses has been that the $\pi \rightarrow \pi^*$ transition is little affected by the halogen, the chief effect being a modest red shift. In support of this assumption, it can be noted that this $\pi \rightarrow \pi^*$ transition is in molecular orbital terms similar to the $\pi \rightarrow \pi^*$ transition in the neutral molecules, and that the halogens are weakly interacting substituents in the neutral-molecule spectroscopy. Halogens perturb the positions and intensities of the neutral ^1L_b transition to only a small extent, and it is reasonable to postulate that this would be equally true for the analogous excited state of the ions.

Conclusions

Photodissociation spectra of halobenzenes and halotoluenes are very similar, indicating at most a minor perturbing role for the methyl group. (For fluorobenzene, however, the ambiguities associated with the transition from one-photon to two-photon kinetics rule out any realistic comparison.)

As expected from theory, the fluorine substituent has no important spectroscopic manifestation. For the heavy-halogen-substituted molecules, the visible peaks are in the positions expected for the strongly allowed $\pi \rightarrow n$ charge transfer transition. These peaks are also in qualitative agreement with the corresponding PES peaks, but the photodissociation peaks for the heavy-halogen derivatives, and particularly iodine derivatives, are significantly blue-shifted from the PES peaks, indicating differing vibrational structure, probably resulting from structural distortion of the ion ground state.

The UV region is expected from theory to show both the first $\pi \rightarrow \pi$ transition (which may be low in intensity), and the first $\pi \rightarrow \pi^*$ transition, lying close together in energy. The broad (or split) UV features are in good accord with this, assuming the $\pi \rightarrow \pi^*$ transition is intense and slightly red-shifted from the unsubstituted toluene position, while the $\pi \rightarrow \pi$ excited state is substantially blue-shifted from toluene ion. The PES spectra are in accord with this interpretation.

Acknowledgments. The support of the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the U.S. Air Force Geophysical Laboratory is gratefully acknowledged. One of us (R.C.D.) is grateful to the Physical Chemistry Laboratory of Oxford University for their hospitality during preparation of the manuscript.

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