Core-electron Spectra of Mono-substituted Benzenes Obtained by the Gas-phase X-Ray Photoelectron Spectroscopy

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The gas-phase X-ray photoelectron spectra were observed on benzene and its eight mono-substituted derivatives; C_6H_5X, X=H, CH_3, NH_2, OH, F, Cl, Br, NO_2 and CN. Binding energies of core levels were determined from the observed spectra by using the spectrum simulation technique, and they were compared with the chemical shift predicted from the CNDO/2 charge densities on the basis of the electrostatic potential model. It is shown that the C1s binding energies of benzene derivatives can be generally correlated with atomic charges, q_j, by the following equation;

$$E_i(\text{C 1s}) = 290.2 + 22.67q_i + \sum_{j\neq i}(q_j/R_{ij}) \quad \text{eV.}$$

By using this relation and the observed C1s binding energies, the atomic charge analysis is carried out. Satellite bands were observed in the C1s spectra as well as in some other core-electron spectra of benzene derivatives. Theoretical calculations are carried out on the energies and probabilities of shake-up transitions. It is concluded that the observed satellites are mainly due to the shake-up processes associated with the excitations of π electrons.

The effects of substituent groups on the charge distributions in benzene derivatives are of great interest from chemical point of view, and have been studied by means of various theoretical methods. However, hitherto, there has been no experimental method which directly gives the atomic charges of a molecule. The core electron binding energies of atoms in a molecule can be determined by means of X-ray photoelectron spectroscopy. It has been well established that the core electron binding energy varies more or less depending on the chemical bonds in the ground state of molecule, and this effect, called "chemical shift," is directly reflecting the charge distribution in the molecule. Thus X-ray photoelectron spectroscopy provides a way to investigate the atomic charges of a molecule.

On several benzene derivatives, Clark *et al.*[1] observed the X-ray photoelectron spectra of their frozen solid states, and discussed the correlation between CNDO/2 charge densities and observed binding energies. In particular, detailed investigations were carried out on fluorobenzenes.[2] In a previous paper,[3] we studied the charge distributions of *p*-benzoquinone, hydroquinone and their halogen-substituted derivatives from the X-ray photoelectron spectra of the solid states of these compounds.

However, the X-ray photoelectron spectrum of a solid sample is unavoidally affected by the so-called solid state effects, so that there always remain some ambiguities in the analyses of chemical-shift data obtained from the solid-state X-ray photoelectron spectroscopy. It is desirable to use the gas-phase X-ray photoelectron spectra in order to study molecular properties. The atomic charges of fluorobenzenes were investigated by Thomas[4] by this technique.

In the present paper, we report the gas-phase X-ray photoelectron spectra of monosubstituted benzenes and the results of the analyses of the observed spectra by means of the electrostatic potential model. We will also report the natures of the satellite bands accompanying the core electron peaks.

Experimental

The gas-phase X-ray photoelectron spectra were measured with a McPherson ESCA 36 electron spectrometer, by employing Mg$K\alpha$ radiation (1253.6 eV), on benzene and its monosubstituted derivatives: C_6H_5X (X=H, OH, NH_2, CH_3, CN, NO_2, F, Cl and Br). Each sample, purified by distillation in advance, was repeatedly out-gassed by the freezing and pumping technique, and then its vapor was introduced into gas-handling system of the spectrometer through a needle valve. In most of the present experiments, the pressure of sample vapor read at the position just after the needle valve, was maintained at about 0.2 Torr. Since this position is considerably separated with fine tubing from the gas-ionization cell of the spectrometer, the actual vapor pressure within the ionization cell must be very much lower, possibly one order less, than the above value.

The binding energies of core electron peaks, referred to the vacuum level, were calibrated by using the N1s peak of nitrogen gas, mixed in the sample vapor, as the reference; the binding energy of the N1s level of nitrogen molecule was taken as 409.9 eV. The energy calibration was repeated at least twice for each sample by independent experiments, and confirmed to be reproducible within 0.2 eV.

Results and Discussion

Binding Energies of Core Electron Levels. In the case of monosubstituted benzenes, there are four inequivalent positions of carbon atom in their benzene rings; we will label these positions as C_1, C_2, C_3, and C_4 as illustrated in Fig. 1. Thus we should expect that C1s levels of a monosubstituted benzene will split into four because of the chemical shifts. In the cases of toluene

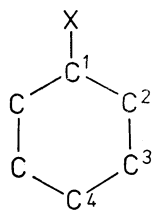

Fig. 1.

TABLE 1. TOTAL CHARGE DENSITIES OF MONOSUBSTITUTED BENZENES OBTAINED FROM CNDO/2 CALCULATION

	Benzene ring							Susbtituents				
	C_1	C_2	C_3	C_4	H_1	H_2	H_3	C	N	O	X[a)]	H
C_6H_6	0.006	0.006	0.006	0.006	−0.006	−0.006	−0.006					−0.006
$C_6H_5CH_3$	0.043	−0.010	0.012	−0.003	−0.008	−0.008	−0.008	−0.021				0.005
$C_6H_5NH_2$	0.137	−0.046	0.026	−0.022	−0.002	−0.008	−0.008		−0.228			0.091
C_6H_5OH	0.196	−0.061	0.032	−0.021	0.001	0.009	−0.008			−0.252		0.143
C_6H_5F	0.236	−0.055	0.028	−0.015	0.018	−0.000	−0.001				−0.199	
C_6H_5Cl	0.085	0.015	0.005	0.013	0.012	0.003	0.001				−0.169	
C_6H_5CN	0.058	0.010	0.006	0.009	0.003	0.000	−0.001	0.084	−0.166			
$C_6H_5NO_2$	0.051	0.011	0.007	0.023	0.036	0.010	0.003		0.471	−0.338		

a) X means halogen atoms

and benzonitrile, there will be another C1s level associated with the carbon atom of substituent group. However, the splittings of C1s levels are not large enough to give well resolved peaks in the observed C1s spectra. In effect, the C1s spectra of monosubstituted benzenes were observed only as a broad and asymmetrical peak with or without a shoulder. Therefore, we used the spectrum simulation technique to determine the binding energy of each C1s level. In applying this technique, we must first determine the peak shape of a single component. The C1s peak of benzene can be used for this purpose since there should be no splitting of C1s level in the case of benzene. In effect, the observed C1s spectrum of benzene gave a sharp symmetrical peak, its width (FWHM) being 1.05 eV under the present experimental condition. We tried to fit the observed peak with a modified Lorentz function described as follows;

$$f(E-E_0) = I\cdot\left[\frac{1-s}{1+\left(\frac{E-E_0}{w/2}\right)^2}+\frac{s}{1+\left(\frac{E-E_0}{w/2}\right)^4}\right] \quad (1)$$

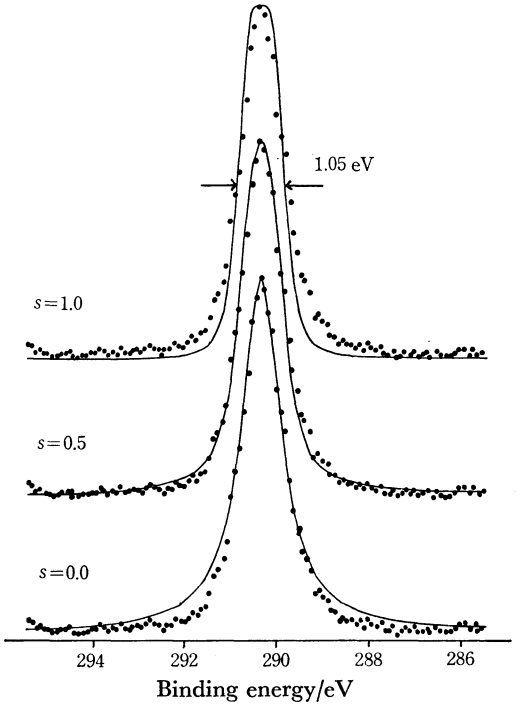

Fig. 2. X-Ray photoelectron spectrum of C1s electrons of benzene. The calculated curve (see text) are shown by solid lines.

where I, E_0 and w are the height, position and width of the peak, respectively, and s is a parameter determining the peak shape. In Fig. 2, the peak shapes calculated for s=0.0, 0.5, and 1.0 are compared with the observed C1s peak of benzene. The best agreement was obtained when s=0.5. Thus we decided to set w=1.05 eV and s=0.5 in the following process. Next, we examined the expected order of different C1s levels of each monosubstituted benzene. This information is desirable to have, though not indispensable, in order to carry out the spectrum simulation procedures. For this purpose, we estimated the relative chemical shift, ΔE_i, from the CNDO/2 charge densities by the following equation given by the electrostatic potential model;[5)]

$$\Delta E_i = k_c q_i + \sum_{j\neq i}(1/R_{ij})\cdot q_j \quad (2)$$

where q_i and q_j are the charge densities of the i-th and j-th atoms, respectively, R_{ij} is the interatomic distance (in atomic units), and k_C is a constant which we tentatively assumed as 22.1 eV/unit charge. The charge densities obtained by CNDO/2 calculations are given in Table 1. In the case of bromobenzene, we did not carry out the CNDO/2 calculation, but assumed that the order of the C 1s levels is the same as in fluorobenzene.

Taking the intensity ratio of the peaks corresponding to C_1, C_2, C_3, and C_4 as 1: 2: 2: 1, we adjusted the peak positions until the best agreement was obtained between the calculated and observed C 1s spectra. The final

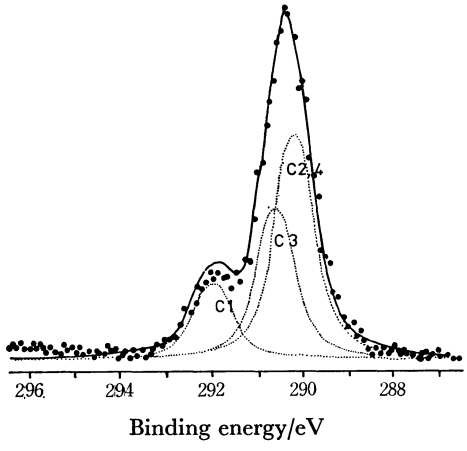

Fig. 3. Decomposition of the C1s spectrum of phenol into the constituent bands. The results of decomposition are shown with broken lines.

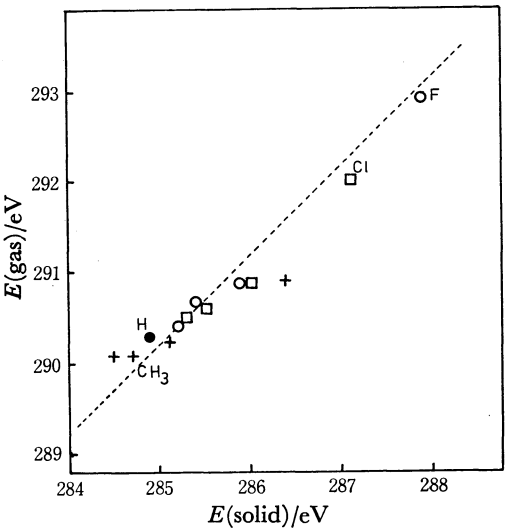

Fig. 4. Comparison of the C 1s binding energies obtained by the gas phase experiments with those reported from the studies of frozen solids.[1]

result of such a procedure is illustrated in Fig. 3, which is the one obtained of phenol. By the above technique, we were able to determine the binding energy of each C 1s level with an accuracy of ± 0.1 eV. The values thus obtained are given in Table 2 together with the binding energies of other core electron levels.

Clark *et al.*[1] reported the C 1s binding energies of benzene, toluene, chlorobenzene and fluorobenzene, obtained from the similar analyses of the shapes of the C 1s spectra of the frozen solid states. In Fig. 4, their values are compared with our gas-phase values. We can conclude that there is a nearly constant energy difference, 5.2 eV, between the solid and gas-phase values. It should be noted first that the solid-state values are the ones referred to the Fermi levels of the samples whereas our gas-phase values are referred to the vacuum level, and second that the binding energy obtained of a solid sample is necessarily affected by the fact that the core-hole ion state is stabilized by polarizing its surroudings. In other words, the binding energies determined from the X-ray photoelectron spectra of solid samples are dependent on the work function and polarization energy of the solid state, both of which should, in principle, vary from sample to sample. Therefore, it is rather surprising to find that the difference between the solid and gas-phase values is almost the same for a variety of monosubstituted benzenes.

Effects of Substituent Group on C 1s Levels. The binding energies of the C 1s levels of monosubstituted benzenes are compared in Fig. 5. We note that, in all cases, the C 1s level of the carbon atom at the substituted position is considerably shifted to higher binding energy as the result of substitution, while those of other carbon atoms of benzene ring show much smaller shifts except in the cases of nitrobenzene and benzonitrile.

As we compare the four molecules, C_6H_5X with X= H, Br, Cl, and F, the shifts of the C 1s level of the atom at the substituted position is the larger as the electronegativity of the substituent atom is the higher. The four substituents, CH_3, NH_2, OH, and F, are mutually

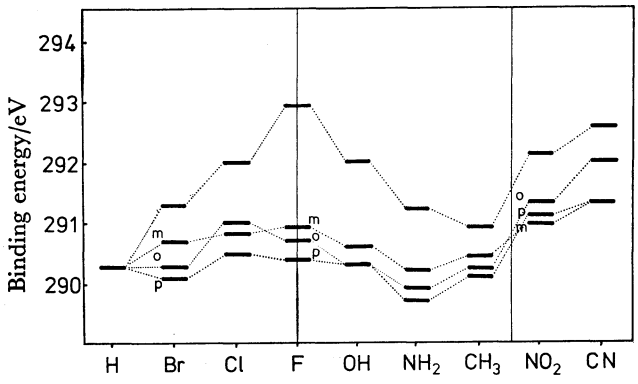

Fig. 5. C 1s Binding energies of benzene derivatives.

isoelectronic, and the electronegativity increases in the order, C<N<O<F. Here again, the core electron level of the carbon atom at the substituted position increases with the increase of electronegativity of the substituent.

In the cases of the six substituents mentioned above, the core electron binding energies of the carbon atoms at *ortho*-, *meta*-, and *para*-positions are in the order, *para*< *ortho*<*meta*, except for chlorobenzene.[6]

The CN and NO_2 groups are known to be electron attractive substituents, whose π-electron systems can interact strongly with those of benzene ring. These can be clearly distinguished from other substituents by looking their effects on the C 1s levels; In benzonitrile and nitrobenzene, all C 1s levels are considerably shifted to higher binding energy as compared with the C 1s level of benzene.

Charge Distribution and Chemical Shift. According to the electrostatic potential model, the binding energy E_i of a core electron level of the i-th atom in a molecule is given by the following equation,

$$E_i = E_0^{\mathrm{A}} + k_{\mathrm{A}} q_i + \sum_{j \neq i} (q_j / R_{ij}) \qquad (3)$$

where E_0^{A} and k_{A} are constants dependent on the kind of atom. Strictly speaking, the value of E_0^{A} must be slightly different for different molecules since it is affected by the molecular reorganization energy, but we could reasonably assume that it remains the same among benzene derivatives.[7]

We can rewrite Eq. (3) in the following form;

$$E_i - \sum_{j \neq i} (q_j / R_{ij}) = E_0^{\mathrm{A}} + k_{\mathrm{A}} q_i \qquad (4)$$

This means that one should obtain a straight line when $E_i - \sum_{j \neq i} (q_j/R_{ij})$ is plotted against q_i. Using the CNDO/2 charge densities and observed C 1s binding energies E_i(obsd), we calculated $E_i(\mathrm{obsd}) - \sum_{j \neq i}(q_j/R_{ij})$ and plotted it against q_i. The result is shown in Fig. 6. We see that the plots are, in effect, well on a straight line except a few points concerned with benzonitrile and chlorobenzene. The inclination of the above straight line gives the value of k_{C} as 22.67 eV/unit charge, which is in good agreement with the value, 22.0 eV/unit charge, calculated from Slater orbitals for the carbon atom by Siegbahn, *et al.*[5] The intercept of the line at $q_i=0$ gives the E_0^{A} value. This found to be 290.2 eV. Thus we obtain the following equation;

Table 2. Binding energies of core levels (unit: eV)

	C_1	C_2	C_3	C_4	C	N	O	X
C_6H_6	290.3	290.3	290.3	290.3				
$C_6H_5CH_3$	290.9	290.2	290.4	290.1	290.1			
$C_6H_5NH_2$	291.2	289.9	290.2	289.7		405.3		
C_6H_5OH	292.0	290.2	290.6	290.2			538.9	
C_6H_5F	292.9	290.7	290.9	290.4				693.3[1]
C_6H_5Cl	292.0	291.0	290.5	290.8				207.5, 206.3[2]
C_6H_5Br	291.3	290.3	290.7	290.1				196.3, 189.3[3]
C_6H_5CN	292.5	292.0	291.3	291.3	291.0	405.0		
$C_6H_5NO_2$	292.1	291.3	291.0	291.1	291.0	411.5	538.3	

1) F 1s, 2) Cl $2p_{1/2,3/2}$ 3) Br $3p_{1/2,3/2}$

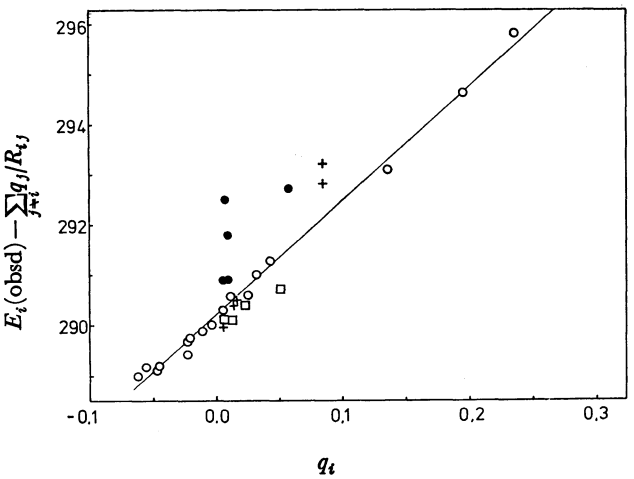

Fig. 6. Correlation of between $E_i(\text{obsd})-\sum_{j\neq i}q_j/R_{ij}$ and q_i.
The data points shown by filled circles, open squares and crosses are those of benzonitrile, nitrobenzene and chlorobenzene, respectively. The data points related with other compounds are shown by open circles.

$$E_i(\text{Cls}) = 290.2 + 22.67q_i + \sum_{j\neq i}(q_j/R_{ij}) \qquad (5)$$

We propose the above equation as the one generally applicable for the analyses of Cls binding energies of benzene derivatives.

By Eq. (5) we calculated the binding energies of Cls levels of monosubstituted benzenes from the CNDO/2 charge densities listed in Table 1, and calculated the Cls spectrum of each compound. The results are compared in Fig. 7. The calculated spectra almost completely agree with the observed ones in the cases of toluene, aniline, phenol and fluorobenzene. In comparison with the above cases, the agreement is less satisfactory in the cases of chlorobenzene, nitrobenzene and benzonitrile. We think that this is reflecting the poor reliabilities of the charge densities estimated for these compounds by CNDO/2 calculations.

Atomic Charge Analysis. According to Eq. (3), the relative chemical shift, $\Delta E_i=E_i-E_0^{\text{A}}$, of each core level can be expressed by a linear combination of charge densities. Thus we have a series of linear equation of the following form;

$$\Delta E_i = \sum_j a_{ij}q_j \qquad (6)$$

In a matrix presentation, they can be summarized as follows

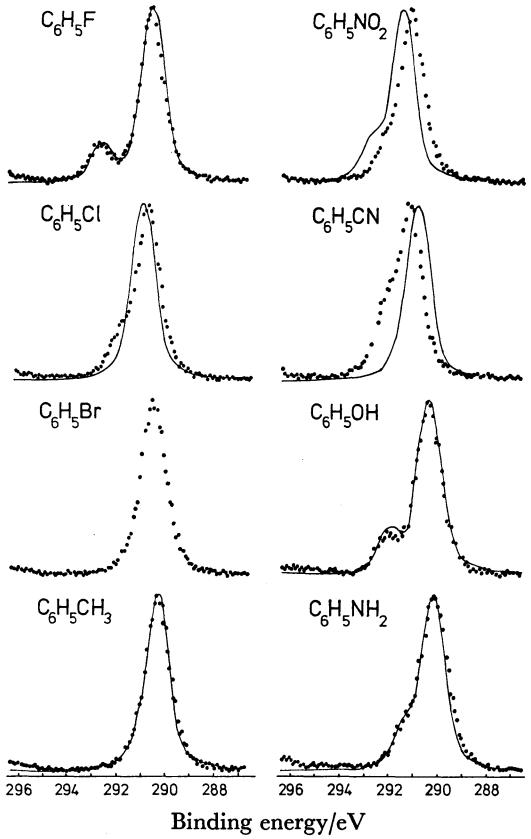

Fig. 7. Cls Spectra of benzene derivatives. The observed data are shown by points. The spectra calculated from the CNDO/2 charge densities are shown by lines.

$$\boldsymbol{\delta} = \mathbf{Aq} \qquad (7)$$

where $\boldsymbol{\delta}$ and $\mathbf{q}$ are vectors whose components are the ordered sets $\{\Delta E_i\}$ and $\{q_j\}$, respectively, and $\mathbf{A}$ is the matrix whose elements are a_{ij}. By comparing Eq. (6) with Eq. (3), one can easily see that an off-diagonal element a_{ij} of $\mathbf{A}$ matrix is equal to $1/R_{ij}$ which can be known from the molecular geometry, and a diagonal element a_{ii} is equal to k_{A}. Thus, if we know the $\boldsymbol{\delta}$ vector, we can, in principle, calculate the $\mathbf{q}$ vector. In other words, the charge densities can be estimated from the observed chemical shifts of core electron levels. This method has been used by several authors[3,4,8] and named "atomic charge analysis" (ACHARGE analysis).

In the preceeding section, we have determined the E_0^{A} and k_{A} values for Cls level, but not for other core levels. Furthermore, the components of $\boldsymbol{\delta}$ vector,

Table 3. Charge densities determined by ACHARGE analysis

	C_1	C_2	C_3	C_4	C	N	O	X
$C_6H_5CH_3$	0.125	−0.042	0.006	0.010	−0.037			
$C_6H_5NH_2$	0.161	−0.044	0.037	−0.042		−0.256		
C_6H_5OH	0.204	−0.034	0.028	−0.040			−0.306	
C_6H_4F	0.265	−0.035	0.032	−0.024				−0.270
C_6H_5Cl	0.161	−0.016	0.061	−0.051				−0.230
C_6H_5Br	0.105	−0.027	0.034	−0.031				−0.086
C_6H_5CN	0.087	0.004	0.008	0.066	0.181	−0.364		

associated with hydrogen atoms are not experimentally available. Thus we have to reduce the dimension of $\boldsymbol{\delta}$ vector by introducing a few assumptions. First, we used the condition of electrical neutrality of molecule, which is expressed as;

$$\sum_j q_j = 0 \tag{8}$$

Second, we assumed that the charge densities of hydrogen atoms are the same as the values obtained by the CNDO/2 calculations, and excluded from the unknown quantities which should be obtained by solving the equation. This assumption may not be legitimate, but seems allowable, since hydrogen atoms of benzene ring are likely to have small charges as indicated by the CNDO/2 calculations (see Table 1), so that the above assumption should not significantly affect the results of ACHARGE analysis. When we use the two assumptions described above, the dimension of $\mathbf{q}$ vector can be reduced to four for aniline, phenol, chlorobenzene, bromobenzene and fluorobenzene, and five for toluene, benzonitrile, and nitrobenzene. Thus we were able to carry out ACHARGE analysis using only the binding energies of C 1s levels in all cases except nitrobenzene. In the case of nitrobenzene, the analysis is possible if we use the N 1s or O 1s binding energy, but we did not carry out the analysis since reliable values of E_0^A and k_A are not available at present for nitrogen and oxygen atoms of benzene derivatives.

The charge densities thus obtained from the analyses of the C 1s spectra of benzene derivatives are listed in Table 3. In most compounds studied here, we found a good agreement between the charge densities derived from the ACHARGE analyses and those by the CNDO/2 calculations. It should be noted that ACHARGE analysis can be carried out without the aid of molecular orbital calculation once the values of E_0^A and k_A have been established. In this sence, we could regard its results as "experimental charge densities."

In Table 4, the results of the ACHARGE analysis of fluorobenzene reported by different authors are compared with those of the present study. They are in satisfactory agreement although the actual procedures of analysis differ a little between different authors.

Table 4. Atomic charges of fluorobenzene

Atom	CNDO/2	ACHARGE analysis		
		Thomas[4]	Clark *et al.*[2]	present work
C_1	0.236	0.23	0.209	0.265
C_2	−0.055	−0.04	−0.028	−0.035
C_3	0.028	0.01	0.005	0.032
C_4	−0.015	0.00	0.003	−0.024
F	−0.199	−0.19	−0.203	−0.270

We note in Table 3 that the net charge on the substituent group (CN) of benzonitrile is negative in agreement with the chemical intuition that CN group is an electron attractive substituent. The situation seems to be not so simple in the case of aniline where the substituent is an electron donative one. As shown in Table 3, the nitrogen atom of the NH_2 group has a considerably large negative charge, so that the net charge on the NH_2 group becomes negative even if we took into account the positive charges on the hydrogen atoms. The same conclusion is derived also from the CNDO/2 charge densities. However, if we examine the π-electron population predicted from the CNDO/2 molecular orbitals, we see that the amount of π electron transferred from NH_2 group to benzene ring amounts to 0.278 *e*. Thus we can conclude that the nitrogen atom of the NH_2 group is donating its π electron to the benzene ring, but attracting σ electron primarily from the carbon atom which is directly bonded to the nitrogen atom, so that the net charge of NH_2 group becomes negative. The situation seems to be more or less similar in the cases of other electron donative substituents.

Satellite Bands of Core Electron Peaks. Core electron peaks of X-ray photoelectron spectra are often accompanied by satellites associated with the two-electron process where an ejection (shake-off) or excitation (shake-up) of an outer-shell electron occurs simultaneously with the photoionization of a core level.[9,10] Figure 8 shows the satellite of the C 1s peak of benzene.

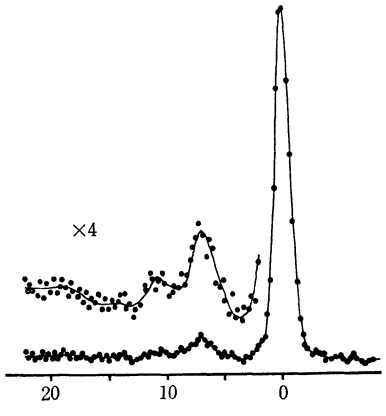

Fig. 8. C 1s Spectrum of benzene. The high-energy region of the spectrum is also shown by expanding the intensity scale to show the satellites. The energy difference from the main peak is given in the abscissa.

We can see two bands in the high binding-energy side of the C 1s peak, their maxima being at 7.0 and 11.0 eV, respectively, from the main peak. The intensity relative to the main peak is 10.5 and 2.5 percent for the 7.0 and 11.0 eV bands, respectively. We examined the pressure dependences of these bands, and confirmed that their energies and intensities relative to the C 1s peak are practically unaffected by the change of the vapor pressure of benzene. This fact indicates that the above bands are not due to the inelastic scattering of photoelectron, but due to the shake-up or shake-off process. Beside the above two bands, we observed several very weak bands at much higher binding energies. For these bands, however, we were not able to confirm whether they are really due to two-electron process or not.

Satellites by two-electron processes were also observed in the C 1s spectra of the monosubstituted benzenes. Their shapes and intensities were found to vary more or less depending on the substituent group. In the case of nitrobenzene, satellite appeared in the O 1s region as well as in the C 1s region, but not in the N 1s region. The O 1s satellite was composed of three bands located at 3.0, 10.0, and 13.0 eV, respectively, from the main peak. A considerably sharp satellite band was observed in the N 1s region of the spectrum of benzonitrile at 5.0 eV from the main peak. No satellite definitely attributable to two-electron process was found in the regions other than C 1s in the cases of other monosubstituted benzenes studied here.

According to the theory based on the sudden approximation, the probability of a shake-up process which yields the final state Ψ_k where a secondary excitation (or ejection) of a valence electron has occurred simultaneously with the photoionization of a core level, can be given as follows;[11]

$$P_k = |\langle \Phi_0 | \Psi_k \rangle|^2 \tag{9}$$

where Φ_0 is the wave function in which the valence-electron orbitals are the same as in the ground state of the molecule without a core hole.

We calculated the molecular orbitals of valence electrons by means of the CNDO/2 method. In order to calculate the molecular orbitals of the core-hole ion, we assumed the localized-core-hole model[12] and used the equivalent-core approximation.[13] The wave functions Φ_0 and Ψ_k were then expressed in the form of a Slater determinant constructed from the above orbitals, and the shake-up probability was calculated by use of Eq. (9). A part of the results thus obtained of benzene are shown in Table 5 in order to illustrate the general trend of the predicted shake-up probabilities. It should be noted that the shake-up probability is predicted to be quite small for σ—σ^* transitions. This was also the case for other σ—σ^* transitions which we have omitted in Table 5. On the other hand, a π—π^* transition ($2b_1 \rightarrow 3b_1$) is predicted to have a considerably large shake-up probability. We carried out similar calculations on monosubstituted benzenes, and found that, like in benzene, the shake-up probability is generally quite small (less than 0.5 percent) in the case of σ—σ^* transition, and the transitions of significant shake-up probability can be found only among π—π^* transitions. Seemingly, the above results are reasonable since we can generally expect that, in a π-conjugated system, π electrons would play the most important role in the relaxation process accompanying the ejection of a core electron because of the labile nature of π electrons.

TABLE 5. SHAKE-UP PROBABILITIES(%) OF C 1s FOR BENZENE OBTAINED BY CNDO/2 CALCULATION

Occupied orbital	Vacant orbital							
	$3b_1(\pi)$	$2a_2(\pi)$	$8a_1$	$9a_1$	$6b_2$	$10a_1$	$11a_1$	$4b_1(\pi)$
$1b_1(\pi)$	0.51	—	—	—	—	—	—	0.06
$3b_2$	—	—	—	—	0.25	—	—	—
$5a_1$	—	—	0.08	0.16	—	0.32	0.0	—
$6a_1$	—	—	0.50	0.17	—	0.08	0.0	—
$4b_2$	—	—	—	—	0.06	—	—	—
$2b_1(\pi)$	5.26	—	—	—	—	—	—	0.09
$5b_2$	—	—	—	—	0.39	—	—	—
$7a_1$	—	—	0.0	0.09	—	0.03	0.08	—
$1a_2(\pi)$	—	0.04	—	—	—	—	—	—

The energy separation of a satellite band from the main core electron peak must be equal to the excitation energy of the core-hole ion. This will be given as follows;

$$\Delta E_k = \langle \Psi_k | H | \Psi_k \rangle - \langle \Psi_0 | H | \Psi_0 \rangle \tag{10}$$

where Ψ_k and Ψ_0 are the wave function of the excited state and that of the ground state of the core-hole ion, respectively. Unfortunately, however, the CNDO/2 method generally provides only poor predictions as regards the energies of π—π^* transitions which are most important to understand the satellites of benzene derivatives. As we have already pointed out, there is a good reason to suppose that, in π-conjugated molecules, the contributions of π electrons are of primary importance in the relaxation process accompanying the ionization of a core level. Therefore, it would be allowable, at least as a first approximation, to attribute the relaxation entirely to π electrons by freezing the states of σ electrons the same as in the initial state without a core hole, and estimate the energies of π—π^* transitions of the core hole ion by means of a semiempirical SCF-MO-CI method within the framework of π electron approximation. Here again, we took the localized-core-hole model. This means that, for a monosubstituted benzene, we have to consider four different core-hole states corresponding to four inequivatent locations of C 1s hole in benzene ring. We carried out the calculation on each of these core hole state. The semiempirical parameters related to the core-hole atoms $C(ls \cdot tr \cdot tr \cdot tr \cdot \pi)$, $N(ls \cdot tr^2 \cdot tr \cdot tr \cdot \pi)$ and $O(ls \cdot tr^2 \cdot tr^2 \cdot tr \cdot \pi)$ were assumed to be the same as those of $N^+(ls^2 \cdot tr \cdot tr \cdot tr \cdot \pi)$, $O^+(ls^2 \cdot tr^2 \cdot tr \cdot tr \cdot \pi)$ and $F^+(ls^2 \cdot 2s^2 \cdot 2p^2 \cdot 2p^2)$, respectively, according to the equivalent-core approximation. We used the Katagiri-Sandrofy's formula[14] for resonance integral and the Nishimoto-Mataga's formula[15] for two-center repulsion integral, and took into account not only the nearest-neighbor resonance integrals, but also the non-nearest-neighbor ones.[16] In the calculations of configuration interactions, we took into account all singly-excited con-

TABLE 6. SHAKE-UP ENERGIES(eV) AND PROBABILITIES(%) OF PHENOL OBTAINED BY π-ELECTRON APPROXIMATION

Transition	Localized core-hole model				Weighted average	Exp.
	C_1	C_2	C_3	C_4		
4→5	4.99(0)	4.69(0.48)	4.51(0.39)	5.53(3.34)	6.81(4.68)	6.8(8.5)
4→6	6.62(0.53)	5.70(0.32)	5.37(0.66)	6.27(0)		
3→5	5.82(4.62)	7.43(2.83)	6.52(1.58)	5.05(0)		
3→6	6.80(0)	7.74(0.00)	7.11(0.11)	6.76(0.47)		
4→7	8.02(0)	7.04(0.01)	7.22(0.03)	7.84(0.05)		
2→5	7.90(0.03)	8.46(0.80)	8.62(1.48)	9.40(0.95)		
3→7	8.64(0.15)	9.41(0.12)	8.91(0.01)	8.19(0)		
2→6	8.54(0)	8.86(0.16)	9.37(0.00)	9.32(0)		
2→7	10.76(0.06)	11.22(0.01)	11.30(0.00)	11.56(0.12)	12.39(2.39)	9.5(2.3)
1→5	13.21(2.56)	12.60(2.00)	12.34(2.57)	12.43(2.26)		
1→6	13.06(0)	12.78(0.00)	12.57(0.00)	12.24(0)		
1→7	15.59(0.01)	15.06(0.01)	14.77(0.01)	14.65(0.10)		

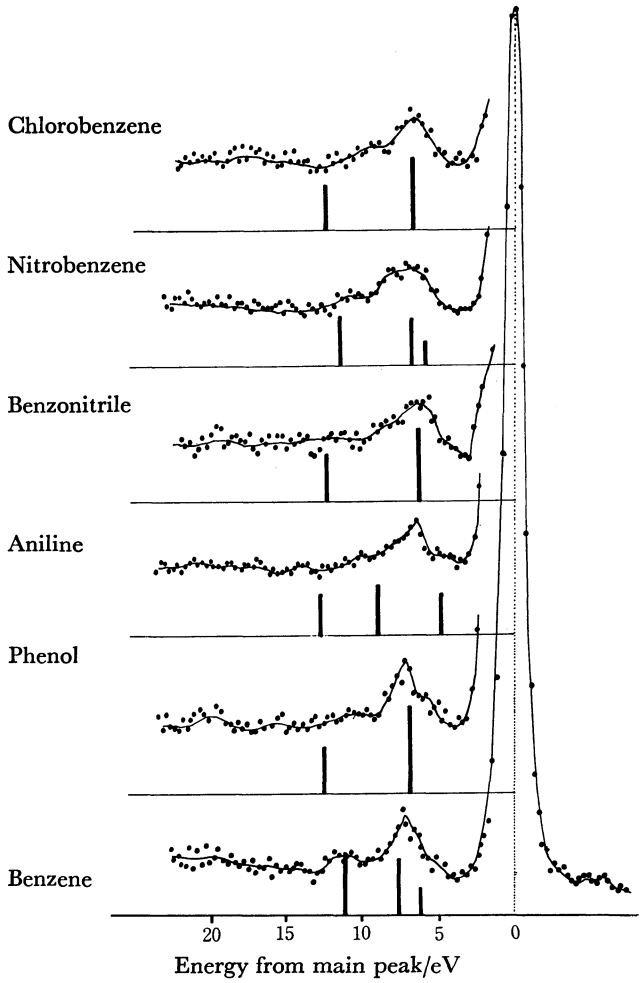

Fig. 9. Satellites accompanying the C ls peaks of X-ray photoelectron spectra of benzene derivatives. Calculated results are shown as vertical bars, whose positions and heights indicate the predicted energies and intensities, respectively.

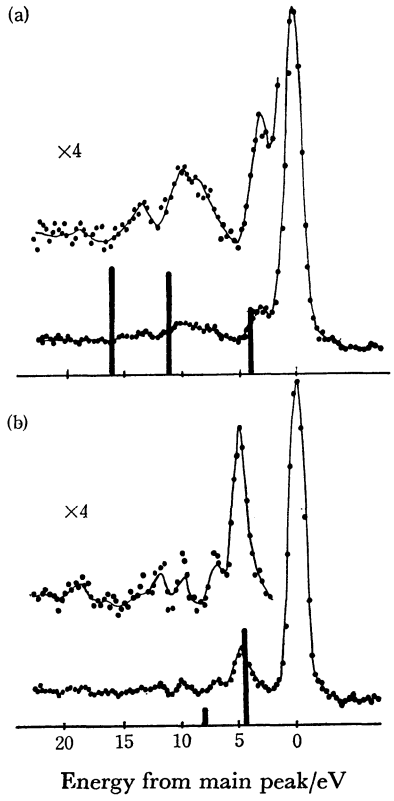

Fig. 10. Satellites accompanying the core electron peaks of the X-ray photoelectron spectra.
(a) O ls spectrum of nitrobenzene (b) N ls spectrum of benzonitrile. Satellite region is shown by expanding the intensity scale.
Calculated results are shown as vertical bars.

figurations. By means of the above method, we estimated the energies of π—π^* transitions of the core-hole state. The shake-up probability was then calculated by Eq. (9) by using the CI wave functions obtained by the above calculations.

The results obtained of phenol are listed in Table 6.

It should be noted that the location of C ls hole does significantly affect not only the transition energies but also the shake-up probabilities. The observed satellite is to correspond to the superposition of the satellites associated with each C ls peak. Unfortunately, however, the resolution of the observed spectrum is not high enough to discuss the fine structures of satellite. Thus, we tentatively took the weighted average of predicted satellites for the purpose to compare with the observed spectra. We see that the predicted satellites are in reasonable agreement with the observation (see Table 6).

Similar calculations were carried out on other monosubstituted benzenes, the results of which are compared in Fig. 9 with the observed satellites. The agreement between the prediction and observation is generally satisfactory. We also performed the calculations on the shake-up satellites of N ls peak of benzonitrile and O ls peak of nitrobenzene. The results are shown in Fig. 10. Here again, we see that the general features of the observed satellites are satisfactorily explained by the calculations.

From the results described above, we can conclude that the prominent satellites accompanying the core electron peaks of the X-ray photoelectron spectra of monosubstituted benzenes are mainly due to the shake-up of π electrons.

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