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X-Ray Photoelectron Spectroscopy of the Molecules Containing the C≡N Group

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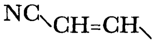
The gas-phase X-ray photoelectron spectra (with Mg*K*α radiation) were observed on acetonitrile, propionitrile, acrylonitrile and fumaronitrile. The ionization potentials were determined for all valence-electron levels of the above molecules by using the data derived from the observed valence-electron bands of X-ray photoelectron spectra and the reported data of ultraviolet photoelectron spectroscopy. It is shown that there is a linear relation between the observed ionization potential (IP) and the CNDO/2 orbital energy (ε): $IP=0.61(-\varepsilon)+3.2$ [eV], for σ-orbitals; $IP=0.38(-\varepsilon)+6.0$ [eV], for π-orbitals. The observed binding energies of the C ls levels were analyzed by means of the electrostatic potential model and the charge densities calculated by CNDO/2 method. Discussion is given also on the shake-up satellite of core-electron peak.

The valence-electron levels of the molecules containing the C≡N group have been investigated by several authors by means of ultraviolet photoelectron spectroscopy (UPS), using He I resonance line as the stimulating radiation.[1–5] However, the informations which have been obtained by these UPS studies, are concerned mainly with the π-electron and lone-pair levels, and little has been known about σ-electron levels, in particular, those of higher ionization potentials.

For investigating valence-electron levels of a molecule, X-ray photoelectron spectroscopy (XPS) provides informations which are complementary to those obtainable by UPS; First, it is possible to investigate with XPS the deep-lying valence-electron levels which can not be studied by UPS, and, second, the prominent bands observable in the valence-electron region of a XPS spectrum are mostly associated with σ-orbitals, whereas, in UPS, π-orbitals usually give strong photoelectron bands.[6]

In the present paper, we report the gas-phase X-ray photoelectron spectra of the molecules containing the C≡N group. The valence-electron bands of the observed spectra will be analysed with the aids of the reported UPS data and the molecular orbital calculations by CNDO/2 method. Discussion will be also given on the core-electron peaks.

Experimental

The gas-phase X-ray photoelectron spectra of acetonitrile CH_3CN, propionitrile CH_3CH_2CN, acrylonitrile $CH_2{=}CH(CN)$ and fumaronitrile  $^{NC}\diagdown CH{=}CH\diagdown_{CN}$ were measured with a McPherson ESCA 36 electron spectrometer, by employing Mg*K*α radiation (1253.6 eV). The purified sample of each compound was out-gassed by the freezing-and-pumping technique in a glass tube connected to the gas-handling system of the spectrometer, and then its vapor was introduced through the gas-handling system into the ionization cell installed in the sample compartment of the spectrometer.[7]

The binding energies of photoelectron peaks, referred to the vacuum level, were calibrated by using the N ls peak (409.9 eV) of the nitrogen gas, mixed with the sample vapor, as the reference. The C ls peak of the sample, induced by the weak Al*K*α radiation which came out as the secondary X-ray from the Al window of the X-ray source, was also used as a subsidiary reference for the calibrations of binding energies of valence-electron bands.

Results and Discussion

Valence-electron Bands. The valence-electron bands of the XPS spectrum of propionitrile is shown in Fig. 1, which exhibits five prominent peaks located at ~13, 17.5, 22.1, 25.2 and 29.7 eV, respectively. Since the propionitrile molecule has twenty two valence electrons, there must be eleven valence-electron levels. The UPS spectrum of propionitrile was studied by Lake and Thompson,[2] who observed seven photoelectron bands, and determined the vertical ionization potentials of the corresponding levels as 12.11, 12.91, 13.64, 13.86, 15.07, 16.59 and 17.46 eV, respectively. Lake and Thompson attributed the 12.11 eV band to the ionizations of the two π-orbitals localized on the C≡N group, and the 12.91 eV band to that of the lone-pair of the N atom, but gave no assignment on other photoelectron bands. Anyway, by the above UPS study, we already know the ionization potentials of eight levels among the eleven valence-electron levels, so that there remain only three levels on which the ionization potential must be determined. As we compare the XPS spectrum with the above UPS data, we note that there are three peaks (at 22.1, 25.5 and 29.7 eV) in the higher-energy region that can not be studied by UPS. Thus, we can safely conclude that these three peaks must be corresponding to the remaining three levels. By this way, we are able to know the ionization potentials of all valence-electron levels.

The relative intensities of valence-electron bands observed by XPS are known to have a relatively simple

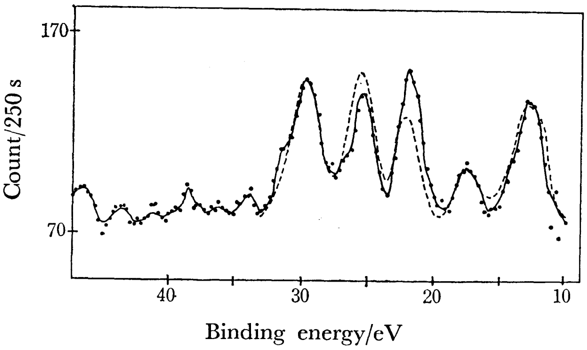


Fig. 1. Valence-electron bands of the XPS spectrum of propionitrile. The final results of simulation (see text) is shown with a broken line.

relation with the wave functions of the ionizing molecular orbitals. According to Gelius *et al.*, this can be approximately expressed as follows;[8]

$$I_j \propto \left(2+\frac{1}{2}\beta\right)\sum_{A\lambda} P_j(A\lambda)\,\sigma_{A\lambda}/\sigma_{C2s} \qquad (1)$$

where $P_j(A\lambda)$ is the atomic population on atom A from the atomic orbital $A\lambda$ in the ionizing molecular orbital j, $\sigma_{A\lambda}$ and σ_{C2s} are the photoionization cross sections of the atomic orbitals, $A\lambda$ and $C2_s$, for X-ray, and β is the asymmetric factor which can be taken as $\beta=2$ for σ-orbitals and -1 for π-orbitals. The relative photoionization cross section has been empirically determined by Gelius and others for various atomic orbitals.[8] The cross section of 2p orbital is reported to be almost one tenth of that of 2s orbital in the cases of the second row elements. Partly because of the small cross sections of 2p orbitals, and partly because of the asymmetric factor, π-orbitals usually have very small photoionization cross sections for X-ray as compared with σ-orbitals, whereas the photoelectron bands associated with π-orbitals strongly appear in the case of UPS. This situation gives us a way to distinguish the photoelectron bands due to π-orbitals from those due to σ- and n-orbitlas by comparing between the UPS and XPS spectra.

We calculated the molecular orbitals of propionitrile by CNDO/2 method, and estimated the relative intensities of XPS bands by using Eq. 1.[9] The results of the above calculations are given in Table 1. According to the calculated intensities, we should expect six prominent peaks in the XPS spectrum of propionitrile. We can safely assign the 22.1, 25.5 and 29.7 eV peaks of the observed spectrum to the 3σ, 2σ and 1σ orbitals, respectively. The 17.5 eV peak is likely to be mainly due to the ionization of the 4σ orbital. Then, we should consider that the band due to the 6σ orbital and the one due to the 7σ (lone pair) orbital are overlapping on each other to be a broad, strong peak at about 13 eV.

Since no peak is observed at 15 eV by XPS, we will attribute the 15.07 eV band observed by UPS, to the ionization of a π-orbital (1π). It is likely that in the XPS spectrum, the band corresponding to the 15.69 eV band of the UPS spectrum, is overlapping on the low-energy tail of the 17.5 eV peak. There remains some ambiguity as regards the assignments of the 13.64 and 13.86 eV bands observed by UPS. We will tentatively assign here the 13.64 eV band to the 2π orbital and the 13.86 eV band to the 6σ orbital. The ionization potential of each molecular orbital thus deduced is given in Table 1.

Using the ionization potentials mentioned above and the calculated relative intensities, we carried out a simulation of the valence electron bands of the XPS spectrum. We assumed here a Gaussian shape for each photoelectron peak, and adjusted peak width so that the best agreement was obtainable with the observed spectrum. The final result of simulation is shown in Fig. 1 with a broken line. We were able to obtain an excellent agreement between the calculated and observed spectra.

The valence-electron bands of the XPS spectrum of acetonitrile is shown in Fig. 2, which shows four peaks at 13.1, 17.3, 25.0 and 29.7 eV, respectively.[6] The situation is much more simple in this case than in the case of propionitrile. Lake and Thompson[2] observed four photoelectron bands (at 12.11, 13.14, 15.5

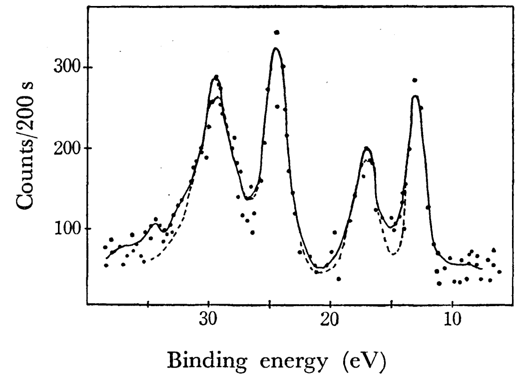


Fig. 2. Valence-electron bands of the XPS spectrum of acetonitrile. The broken line is the result of simulation.

Table 1. Molecular orbitals of propionitrile

	CNDO/2		Orbital[5] energy (*ab initio*) [eV]	*IP* (obs.)[eV]		
	Orbital energy[eV]	Relative intensity		UPS[2]	XPS	(Peak width[eV])
4π (C≡N)	−15.43	0.07	−12.92	12.11		
3π (C≡N)	−15.76	0.11	−12.92			
7σ	−16.22	0.31	−14.86	12.91	~13	
2π	−18.57	0.07	−15.08	13.64		
6σ	−18.74	0.67	−15.38	13.86		
5σ	−21.71	0.16	−16.24	16.59		
1π (pseudo π)	−25.38	0.06	−18.36	15.07		
4σ	−25.41	0.39			17.5	
3σ	−31.60	1.00[a]			22.1	(2.5)
2σ	−38.51	1.91			25.5	(1.8)
1σ	−43.23	1.78			29.7	(2.2)

a) Assumed as the reference.

TABLE 2. MOLECULAR ORBITALS OF ACETONITRILE

	CNDO/2		IP (obsd) (eV)		
	Orbital energy[eV]	Relative intensity	UPS[2]	XPS	(Peak width[eV])
2π (e) π(C≡N)	−15.98	0.11	12.11	—	
4σ (a_1) n(N atom)	−17.25	0.42	13.14	13.14	(1.6)
3σ (a_1) σ	−22.90	0.55	~17	17.3	(2.4)
1π (e) mainly pseudo-π(CH_3)	−23.25	0.09	15.5	—	
2σ (a_1) σ	−36.51	1.00[a]	25.0	25.0	(2.2)
1σ (a_1) σ(mostly s-character)	−40.92	1.36		29.7	(3.6)

a) Assumed as the reference.

TABLE 3. MOLECULAR ORBITALS OF ACRYLONITRILE

	CNDO/2		IP (obsd) [eV]		
	Orbital energy[eV]	Relative intensity	UPS[2]	XPS	(Peak width[eV])
3π (out of plane)	−14.35	0.05	10.91	—	
7σ	−15.85	0.09	13.56		
2π (in plane, C≡N)	−16.35	0.08	12.36	~13.3	
6σ (lone pair)	−18.87	0.35	13.04		
1π (out of plane)	−21.34	0.05	14.43	—	
5σ	−21.42	0.19	16.17	~17.5	
4σ	−27.43	0.13	17.62		
3σ	−29.73	0.53		21.3	(2.0)
2σ	−38.96	0.95		25.3	(3.1)
1σ	−42.76	1.00[a]		29.7	(3.2)

a) Assumed as the reference.

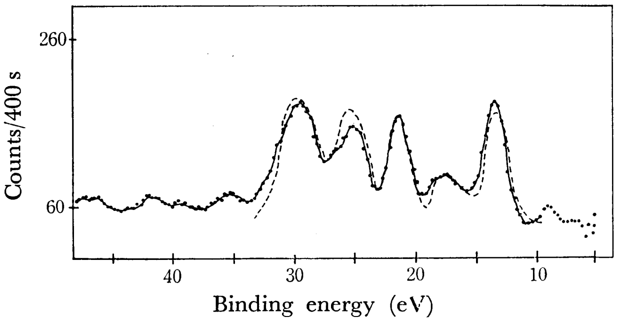


Fig. 3. Valence-electron bands of the XPS spectrum of acrylonitrile. The broken line is the result of simulation.

and about 17 eV) by UPS. By combining the above UPS data with our XPS ones, we can directly derive the ionization potentials of the six valence-electron levels of acetonitrile as 12.11, 13.14, 15.5, 17.3, 25.0 and 29.7 eV. At the same time, we can conclude that the 12.11 and 15.5 eV levels are of π-type since the bands associated with these levels do not appear in the XPS spectrum.

The orbital energies and relative intensities obtained by the CNDO/2 calculations are listed in Table 2. We will assign the 12.11 eV band observed by UPS to the ionization of the doubly-degenerated π-electron level, localized on the C≡N group, as reported by Lake and Thompson, and the 13.4 eV band to that of the lone pair. Then, other photoelectron bands can be assigned as shown in Table 2, assuming the sequence of levels as predicted by the CNDO/2 calculation.

The result of the simulation of the valence-electron bands of the XPS spectrum is shown in Fig. 2 with a broken line. Here, again, we obtained an excellent agreement between the calculated and observed spectra.

In the case of acrylonitrile, the ionization potentials are already known on seven levels among the total ten valence-electron levels through the UPS study by Lake and Thompson,[2] the reported values of the vertical ionization potentials being 10.91, 12.36, 13.04, 13.56, 14.43, 16.17 and 17.62 eV, respectively. By means of XPS, we can observe three prominent peaks at 21.3, 25.3 and 29.7 eV, in the region above 18 eV (see Fig. 3). Combining the above data, we were able to know the ionization potentials of all valence-electron levels.

The results of CNDO/2 calculations on acrylonitrile are shown in Table 3. According to Lake and Thompson, the 10.91 eV of the UPS spectrum is due to the π(C=C) orbital, and the 12.36 eV band to the π(C≡N) orbital. They assigned the 13.04 eV band to the ionization of the lone pair of the N atom. Thus we will attribute the 10.91, 12.36 and 13.04 eV bands to the 3π, 2π and 6σ orbitals, respectively. The calculation predicts a considerably high intensity for the 6σ band in the XPS spectrum. This is consistent with the observation which shows a prominent peak at about 13.3 eV. It is not possible to obtain a definite conclusion concerning the assignment of the 13.56 and

TABLE 4. MOLECULAR ORBITALS OF FUMARONITRILE

CNDO/2			IP (obsd) [eV]		
	Orbital energy[eV]	Relative intensity	UPS[3]	XPS	(Peak width[eV])
$5\pi(2a_u)$(out of plane)	−13.80	0.08	11.15	—	
$4\pi(6a_g)$(in plane)	−15.81	0.07	12.78	—	
$9\sigma(5a_g)$(partially, lone pair)	−16.21	0.32	(13.44)	—	
$3\pi(5b_u)$(in plane, $C\equiv N$)	−17.68	0.11	13.10	—	
$8\sigma(4b_u)$(lone pair)	−18.38	0.70	13.44	13.4	
$2\pi(1b_g)$(out of plane, $C\equiv N$)	−19.54	0.09	13.67	—	
$7\sigma(4a_g)$	−20.34	0.70	15.62	15.6	
$1\pi(1a_u)$(out of plane)	−23.01	0.08	14.41	—	
$6\sigma(3a_g)$	−24.07	0.43	18.2	18.0	(1.4)
$5\sigma(3b_u)$	−28.79	0.27	19.7	~20	(1.4)
$4\sigma(2b_u)$	−32.10	1.00		22.2	(1.4)
$3\sigma(2a_g)$	−39.05	1.58		25.6	(1.4)
$2\sigma(1b_u)$	−40.94	1.79		28.5	(2.5)
$1\sigma(1a_g)$	−44.47	1.64		30.2	(2.5)

a) Assumed as the reference.

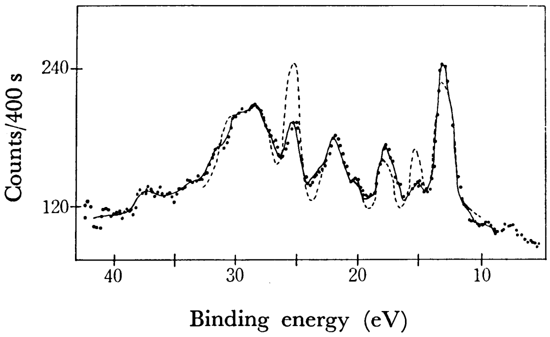


Fig. 4. Valence-electron bands of the XPS spectrum of fumaronitrile. The broken line is the result of simulation.

14.43 eV bands of the UPS spectrum. One of them must correspond to the 7σ orbital and the other to the 1π orbital. We tentatively assigned the 13.56 eV band to the 7σ orbital and the 14.43 band to the 1π orbital, since this assignment gave a better result in the simulation of the valence-electron bands of the XPS spectrum as compared with the alternative assignment. Seemingly, the weak band at about 17.5 eV in the XPS spectrum is due to the superposition of the two bands due to the 5σ and 4σ orbitals, which were separately observed by UPS at 16.17 and 17.62 eV.

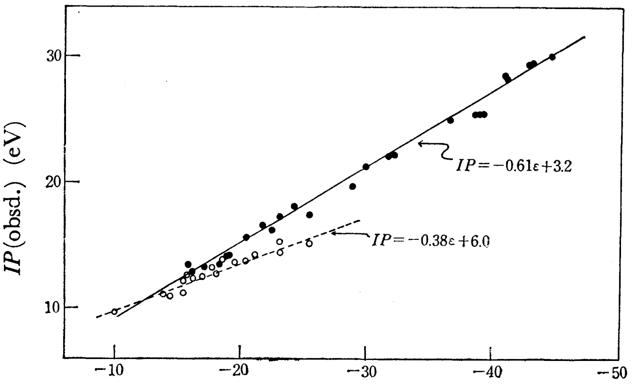
We carried out the simulation of the XPS spectrum using the ionization potentials discussed above and the calculated intensities, and were able to obtain a good agreement between the calculated and observed spectra, as shown in Fig. 3.

As shown in Fig. 4, eight peaks were observed in the valence-electron region of the XPS spectrum of fumaronitrile, their maxima being located at 13.4, 15.6, 18.0, ~20, 22.2, 25.6, 28.5 and 30.2 eV, respectively. The UPS spectrum of fumaronitrile was studied by Bock and Stafast,[3] who observed nine photoelectron bands at 11.15, 12.78, 13.10, 13.44, 13.67, 14.41, 15.62, 18.2 and 19.7 eV, respectively, and carried out the assignments of these UPS bands on the bases of the analysis of vibrational structure and the molecular orbital calculation by extended Hückel method. By comparing the above UPS data with our XPS ones, we can conclude that the 11.15, 12.78, 13.10, 13.67 and 14.41 eV bands observed by UPS are due to the ionization of the π-orbitals because they are missing in the XPS spectrum.

The results of our CNDO/2 calculations are given in Table 4. The first strong peak at 13.4 eV in the XPS spectrum must correspond to the 13.44 eV photoelectron band observed by UPS, which was assigned to the ionization of the lone-pair. In effect, the 8σ orbital which has a character of the lone-pair orbital, is predicted to have a large photoionization cross section for X-ray. In the XPS spectrum, we can not find a peak corresponding to the ionization of the 9σ orbital. Seemingly, it is overlapping on the 13.4 eV peak. Assuming the sequence of other σ-orbitals as predicted by the CNDO/2 calculation, we will attribute the 30.2, 28.5, 25.6 and 22.2 eV peaks to the 1σ, 2σ, 3σ and 4σ orbitals, respectively. Since the 5σ orbital is predicted to have a relatively small intensity, we will attribute the weak peak at about 20 eV to the ionization of the above orbital. Then, the 18.0 and 15.6 eV peaks are attributable to the 6σ and 7σ orbitals. For the UPS bands associated with the π-orbitals, we will adopt the assignments given by Bock and Stafast since their results are consistent with our CNDO/2 calculation as regards the sequence of the orbitals. The ionization potential thus derived for each orbital is shown in Table 4.

The results of the simulation of the valence bands of the XPS spectrum is shown in Fig. 4 with a broken line, which is in a good agreement with the observed spectrum, except that the 15.6 and 25.6 eV peaks are predicted a little too strongly.

The results shown in Tables 1—4, clearly indicate that the observed ionization potentials are considerably



Orbital energy (CNDO/2) (eV)

Fig. 5. Relation between ionization potential and CNDO/2 orbital energy: Filled circles are the data concerned with σ-orbitals, and open circles are those concerned with π-orbitals.

different from the values which are expected from the calculated orbital energies according to the Koopmans' theorem; the discrepancy between them is larger for deeper orbitals. In several UPS studies, it was mentioned that a reasonable value of ionization potential is obtainable when 4 eV is subtracted from the value given by Koopmans' theorem from the CNDO/2 orbital energy. However, the present data demonstrate that the above method is not satisfactory, in particular, for deeper orbitals.

In Fig. 5,[10] observed ionization potentials are plotted against CNDO/2 orbital energies. In this figure, the data concerned with π-orbitals are shown as open circles and those concerned with σ- and n-orbitals are shown as filled circles. Interestingly, the latters fall on a straight line and formers on another straight line. The relationship between the ionization potential (IP) and CNDO/2 orbital energy (ε) can be described as follows; for σ-orbitals,

$$IP = 0.61(-\varepsilon) + 3.2\ [\mathrm{eV}] \tag{2}$$

and, for π-orbitals,

$$IP = 0.38(-\varepsilon) + 6.0\ [\mathrm{eV}] \tag{3}$$

Probably, the above difference between the relation for σ-orbitals and that for π-orbitals is reflecting the problems concerned with the semiempirical parametrization in CNDO/2 method. It is also possible that the above difference is partly due to the difference in relaxation energy between σ- and π-orbitals. It should be noted that, because of the above relations between IP and ε, the locations of π-electron levels relative σ-electron levels are often incorrectly predicted by CNDO/2 method. This should be kept in mind when the results of CNDO/2 calculations are used for the assignment of photoelectron bands. The empirical relations, Eqs. 2 and 3, could be used to obtain the correct locations of valence electron levels, at least, in the cases of the molecules similar to those studied here.[11]

Core-electron Spectra. In all of the molecules studied here, one can generally expect that the charge density on the carbon atom of the C≡N group must be significantly different from those of other carbon atoms, and this difference of the charge densities will arise a relatively large splitting between the C 1s peak due to the former carbon atom and those due to the latter ones. However, the observed C 1s spectrum of each compound showed a single peak without a shoulder, although it is a little broad and asymmetric as illustrated by the spectra of propionitrile and fumaronitrile, shown in Fig. 6. This fact implies that the splitting of C1s levels must be smaller than 0.6 eV in all molecules studied here.

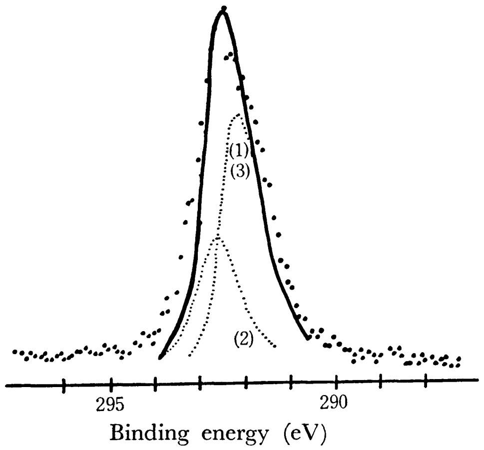


Fig. 6(a). C 1s peak of propionitrile. The observed data are shown by points. The solid line indicates the calculated peak shape which is obtained by superposing peaks due to different C 1s levels, illustrated with dotted lines. Their splitting being assumed as predicted from the CNDO/2 charge densities (see text). The peak number (i) is due to i-th C 1s (i= 1,2,3) (see Table 5).

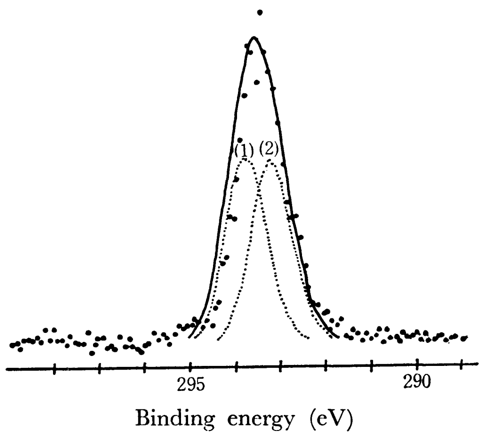


Fig. 6(b). C 1s peak of fumaronitrile. The observed data are shown by points. The solid line indicates the calculated peak shape which is a superposition of the two C 1s peaks shown with dotted lines. The peak number (1) is due to C(1) and (2) to C(2) (see Table 5).

The net charge on each carbon atom, calculated by CNDO/2 method, is given in Table 5, where we can see that the carbon atom of the C≡N group has a charge of about +0.09 e whereas the net charges on other carbon atoms are −0.02 e∼+0.02 e. According to the electrostatic potential model, the binding energy (E_i) of a core-electron level of the i-th atom can be

Table 5.

		q_i	ΔE [eV]	$\langle\Delta E\rangle$ [eV]	E_{obsd} [eV]	E_0 [eV]
$\overset{(2)}{C}H_3\overset{(1)}{C}N$	C_1	+0.090	0.71	0.55	293.1	292.5
	C_2	−0.023	0.38			
$\overset{(3)}{C}H_3\overset{(2)}{C}H_2\overset{(1)}{C}N$	C_1	+0.085	0.54	0.72	292.4	291.7
	C_2	+0.017	1.07			
	C_3	+0.002	0.54			
$\overset{(3)}{C}H_3=\overset{(2)}{C}H(\overset{(1)}{C}N)$	C_1	+0.092	0.47	0.51	292.5	292.0
	C_2	+0.010	0.70			
	C_3	−0.022	0.35			
$CH(CN)=\overset{(2)}{C}H(\overset{(1)}{C}N)$	C_1	+0.089	1.35	1.35	293.5	292.4
	C_2	+0.021	0.81			

related to the charge densities on the atoms in the molecule by the following equation,

$$E_i = E_0 + kq_i + \sum_{i \neq j} (q_j/R_{ij}) \tag{4}$$

where E_0 and k are the constants depending on the kind of atom, q_i and q_j are the charge densities on the i-th and j-th atoms, respectively, and R_{ij} is the interatomic distance.[13] In a previous paper, we showed that the binding energies of the C 1s levels of monosubstituted benzenes can be expressed as follows;[14]

$$E_i = 290.2 + 22.67\,q_i + 14.39 \sum_{i \neq j} (q_j/R_{ij}) \text{ [eV]} \quad (R_{ij}\text{; in Å}) \tag{5}$$

thus E_0=290.2 eV and k=22.67 eV/unit charge. We can assume the same k value for the C 1s levels of the present molecules, but the value of E_0 could be different in the present cases since it depends, to some extent, on the relaxation energy.

We calculated the relative chemical shift of each C 1s level in a molecule by the following equation,

$$\Delta E_i = E_i - E_0 = 22.67 q_i + 14.39 \sum_{j \neq i} (q_j/R_{ij}) \tag{6}$$

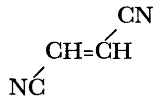
The results are given in Table 5. In all molecules studied here, the difference between the relative chemical shifts of the C 1s levels is predicted to be less than 0.6 eV. This implies that the splitting of the C 1s levels is less than 0.6 eV in agreement with the results of observation. In effect, when we simulated the C 1s peak shape, by using the calculated relative chemical shifts, a good agreement was obtained in all cases between the observed and predicted peak shape as shown in Fig. 6.

If we consider that the binding energy of the observed C 1s peak gives the average of the binding energies of the C 1s levels in the molecule, we can derive the following relation.

$$E_0 = E_{obsd} - \langle\Delta E\rangle \tag{7}$$

where $\langle\Delta E\rangle$ is the average of the relative chemical shifts calculated by Eq. 6. Using the observed C 1s binding energy and the calculated $\langle\Delta E\rangle$, we estimated E_0 for each compound. The results are given in the last column of Table 5. Note that the E_0 values thus obtained are about 292 eV in all cases. The above values are about 2 eV larger than the E_0 value which we have previously obtained for the monosubstituted benzenes. As we have already mentioned, E_0 is dependent partly on the relaxation energy which should, in principle, vary depending on the electronic structure of each molecule. One might reasonably assume that the contribution of relaxation energy is nearly the same for the molecules of the same type as in the case of monosubstituted benzenes. However, it can be appreciably different for the type of molecules studied here from that for benzene derivatives. Seemingly, the difference between the E_0 value obtained in the present study and that previously obtained for benzene derivatives, demonstrates the importance of the contribution of the relaxation energy.

Table 6. N1s binding energy and CNDO/2 charge of the N atom of C≡N group

	N1s binding energy [eV]	CNDO/2 charge
CH_3CN	405.6	−0.160
CH_3CH_2CN	405.3	−0.162
$CH_2=CH(CN)$	405.3	−0.152
	405.9	−0.140
C_6H_5CN	405.0	−0.166
(N_2	409.9	0.000)

For the four molecules studied here, one can not expect a splitting of N 1s level. In effect, N 1s spectrum appeared as a single sharp peak. The observed binding energies are given in Table 6. As compared with the N 1s binding energy of the nitrogen molecule (409.9 eV), the observed N 1s binding energy is smaller by more than 4 eV in the cases of acetonitrile, propionitrile and acrylonitrile, and by 3 eV in the case of fumaronitrile. This fact indicates that the nitrogen atoms of the C≡N group is negatively charged by considerable amount. This is consistent with the results of CNDO/2 calculation.

Core-electron peaks of XPS spectra are often accompanied by satellites associated with the shake-up or shake-off transitions. In the present study, a prominent satellite was able to be observed only in the case of the N 1s peak of fumaronitrile. In this case, a satellite band is at 4.5 eV from the main N 1s peak as shown in Fig. 7.

According to the theory based on the sudden approximation, the relative probability of a shake-up process which yields the final state Ψ_k where a secondary

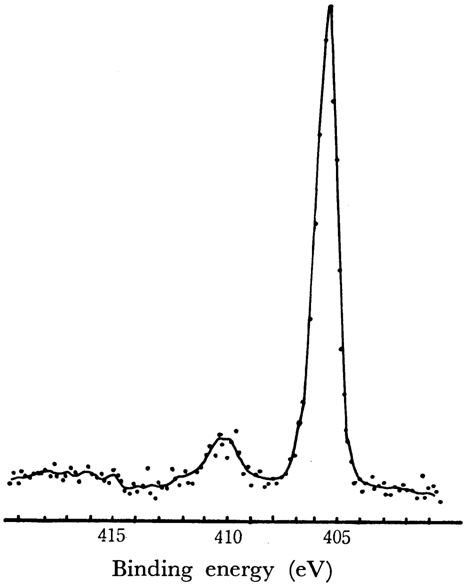


Fig. 7. N 1s spectrum of fumaronitrile: Note that there is a satellite peak at 4.5 eV from the primary peak.

excitation of a valence electron has occurred simultaneously with the photoionization of a core-electron level, can be given as follows;

$$P_k = |\langle \Phi_0 | \Psi_k \rangle|^2$$

where Φ_0 is the wave function of the core-hole ion, in which the valence-electron orbitals are taken the same as in the neutral molecule. By using the molecular orbitals obtained by CNDO/2 method,[15] we estimated the relative probabilities of various shake-up processes. In agreement with the observation, the above calculations predict the presence of a strong shake-up satellite only for the N ls peak of fumaronitrile. In this case, the shake-up process associated with the lowest π-π^* transition was predicted to have probability of 10.8% relative to the total photoionization cross section of the N ls level. No shake-up process is predicted to have a relative probability of more than 5% for the photoionizations of the C ls levels of the same molecule. In the cases of the orther three molecules, all shake-up processes were predicted to have a relative probability of less than 5% for the ionizations of the C ls levels as well as for those of the N ls levels.

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7) The pressure of the sample vapor, read just after the needle valve of the gas-handling system was about 0.2 Torr. The actual vapor pressure in the ionization chamber is likely to be one order less than the above value.

8) For example, refer the following paper; U. Gelius and K. Siegbahn, *Faraday Discuss. Chem. Soc.*, **54**, 257 (1972).

9) We used Gelius' values for the relative cross sections of atomic orbitals.

10) The results obtained in our previous work on the UPS spectra of tetracyanoethylene and tetracyano-*p*-quinodimethane,[4] are also included in this figure.

11) On fluoromethanes, the following relation was given by Shirley *et al.*[12] between the observed ionization potential and the CNDO/2 orbital

$$IP = 0.8(-\varepsilon)$$

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15) The equivalent-core approximation was used to calculate the molecular orbitals of the core-hole ions. The method of calculation was described in our previous paper.[14]