X-Ray Photoelectron Spectroscopy of Chloromethanes and Chloroethanes

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(Received May 15, 1976)

X-Ray photoelectron spectra of chloromethanes ($CH_{4-n}Cl_n$, $n=2,3,4$) and chloroethanes ($CH_3CH_{3-n}Cl_n$, $n=1,2,3$) in vapor phase were observed employing Mg *Kα* radiation. The observed Cls binding energies were analyzed by means of Siegbahn's electrostatic potential model and charge densities calculated by the CNDO/2 method, and the effects of inclusion and exclusion of Cl 3d atomic orbitals in the basis set of the CNDO/2 calculation is critically investigated. The assignment of all valence electron levels of above molecules were performed with the aids of the CNDO/2 calculations incorporated with Gelius' intensity model and the reported data of ultraviolet photoelectron spectroscopy.

X-Ray photoelectron spectroscopy (XPS) of free molecules in gas phase provides various useful informations concerning molecular electronic structures. By means of XPS, one can directly determine core-electron binding energies, which reflect charge distribution in molecule. As for valence-electron levels, XPS offers informations complementary to those obtainable by ultraviolet photoelectron spectroscopy (UPS) which employs the He I or He II line as the stimulating radiation; deep valence-electron levels, out of reach of UPS, are able to be studied by XPS, and, from the comparison between XPS and UPS spectra, one can obtain information concerning the s- and p-characters of ionizing molecular orbitals.

From the above point of view, we have previously investigated the gas-phase X-ray photoelectron spectra of mono-substituted benzenes,[1)] and those of a series of molecules containing the C≡N group.[2)]

In the present paper, we will describe the results obtained by gas-phase XPS of chloromethanes, $CH_{4-n}Cl_n$ (n=2, 3, and 4) and chloroethanes, $C_2H_{6-n}Cl_n$ (n=1, 2, and 3). On those series of chlorine-containing molecules, UPS studies have been carried out by other authors,[3)–7)] but no systematic investigation by gas-phase XPS has been hitherto reported.

We examined the correlation of the chemical shifts of Cls levels and charge distributions calculated by the CNDO/2 method. Discussion will be given on the effects of inclusion and exclusion of vacant 3d atomic orbitals of chlorine in the CNDO/2 calculations. We also intended to elucidate all of the valence-electron levels in these molecules from the analysis of XPS spectra with the aids of the reported UPS data and the CNDO/2 calculations.

Experimental

All materials used here were commercially obtained, and purified by distillation.

The gas-phase XPS spectra were measured with McPherson ESCA 36 electron spectrometer, equipped with a gas-iozination cell and gas-control system, by employing Mg *Kα* (1253.6 eV) as the stimulating radiation. Details of experimental procedure were the same as those described in our previous papers.[1,2)]

Binding energies of core-electron peaks were calibrated by using the Nls peak of nitrogen gas (409.9 eV) mixed in sample vapors as the reference. The weak Al *Kα* radiation (1486.6 eV) which came out as the secondary X-ray from the Al window of the gas-ionization cell, gave weak core-electron peaks at the kinetic energies exactly higher by 233.0 eV than the kinetic energies of the corresponding peaks by Mg *Kα*. Some of them are located closely to the valence-electron spectrum due to Mg *Kα*. For example, Cl 2s peak induced by Al *Kα* appears at the position corresponding to the binding energy of about 45 eV in the spectrum by Mg *Kα*. Thus we used this peak as a subsidiary reference for the calibration of binding energies of valence-electron peaks.

Measurement was carried out at least twice for each sample. Binding energies thus determined were reproducible within ±0.1 eV.

Results

For each material, we carried out measurement both for core- and valence-electron regions. In order to illustrate the general features of the XPS spectra of the chlorine-containing molecules studied here, three regions of the spectrum of chloroform are shown in Fig. 1. Note that the Cl 2s peak is apparently broader than C 1s peak, and that the C 1s and Cl 2s peaks induced by Al *Kα* appear in the spectrum of valence-electron region.

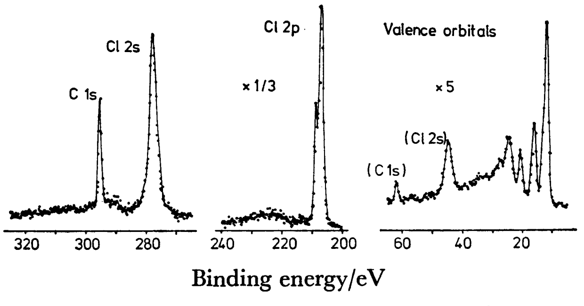
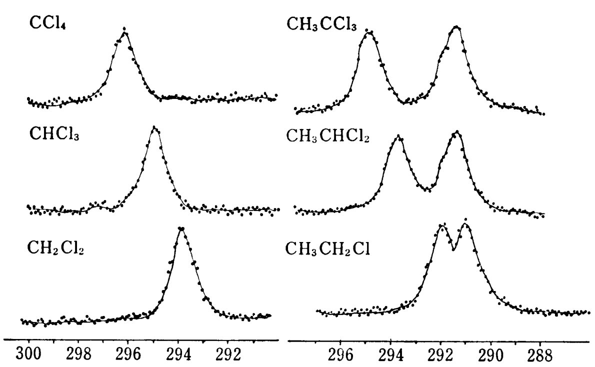


Fig. 1. Core and valence electron spectra of chloroform.

The C 1s spectra of chloromethanes and chloroethanes, observed with a higher resolution, are shown in Fig. 2. In the case of chloromethanes, the C 1s peak is markedly shifted to higher binding energy on increasing the number of chlorine atoms in a molecule, as it is expected from the high electronegativity of chlorine. In the case of chloroethanes, C 1s spectrum splits into two peaks of equal intensity, in which the one at higher binding energy (C 1s (*a*)) is attributable to the carbon atom of chlorine-substituted methyl group (hereafter, we denote this carbon atom as C(*a*)), and the one at lower binding energy (C 1s (*b*)) to the other carbon atom (we denote it as C(*b*)). C 1s (*a*) peak shows a marked shift



(a) chloromethanes (b) chloroethanes

Binding energy/eV

Fig. 2. C 1s spectra of (a) chloromethanes and (b) chloroethanes.

to higher binding energy on increasing the number of substituted chlorine atoms. The extent of this shift is almost the same as that found for the corresponding chloromethane.

As compared with the above change of C 1s binding energy, the changes of Cl2s and Cl2p binding energies are quite small, although these binding energies slightly increase with the number of chlorine atoms. The determined binding energies of core-electron levels are listed in Table 1.

TABLE 1. OBSERVED CORE ELECTRON BINDING ENERGIES OF CHLOROMETHANES AND CHLOROETHANES (eV)

	C 1s	Cl 2s	Cl $2p_{3/2}$
CH_3Cl	(292.4)*	(277.2)*	
CH_2Cl_2	294.0 (293.9)	277.6 (277.6)	206.7
$CHCl_3$	295.1 (295.1)	277.8 (277.7)	206.8
CCl_4	296.3 (296.3)	278.0 (278.0)	207.0
CH_3CH_2Cl	292.1, 291.1	276.8	206.0
CH_3CHCl_2	293.8, 291.5	277.2	206.4
CH_3CCl_3	295.0, 291.5	277.3	206.5

*) Figures in parentheses are from Thomas (Ref. 8).

Full width of half maximum (ΔE_{fwhm}) of C 1s peak was observed to be 1.2, 1.05, and 1.05 eV for dichloromethane, chloroform, and carbon tetrachloride, respectively. ΔE_{fwhm} of 1.05eV is likely to be the resolution limit under the present experimental condition, so that, among the above three cases, the C 1s peak of dichloromethane only can be concluded to be broader than the instrumental broadening. In the case of chloroethanes, ΔE_{fwhm} of C 1s (*a*) peak is almost constant at 1.1 eV, which is close to the resolution limit, but C 1s (*b*) peak is markedly asymmetric with ΔE_{fwhm} of about 1.3 eV, exhibiting a shoulder at about 0.4 eV from the main peak. The above asymmetry of C 1s (*b*) peak is very similar to that of the C 1s peak of methane reported by Gelius,[9] who explained the above asymmetry of the C 1s peak of methane as the effect of vibrational structure. It is also noteworthy that ΔE_{fwhm} of Cl 2s is as large as 2.6 eV. This can be attributed to the life-time broadening associated with the Coster-Kronig process.

It is of large value to know relative photoionization cross sections of core-electron levels, both from theoretical interest and from the interest to use XPS as a tool of quantitative analysis. However, as it has been pointed out by Siegbahn *et al.*,[10] relative intensities of photoelectron peaks could change, more or less, depending on the pressure of sample vapor, because of the effect of inelastic scattering. This pressure dependence of relative intensity is significant at higher sample pressure, but becomes almost negligible at sufficiently low pressure. We previousely observed the pressure dependence of the intensity ratio of the O 1s and C 1s peaks of methanol,[11] and found that the ratio was independent of sample pressure within the pressure region usually used in our experiments. By adopting such an experimental condition, we compared the integrated intensities of Cl 2s, Cl 2p, and C 1s peaks in the XPS spectra of chloromethanes and chloroethanes, and found that the relative intensities of these peaks can be quantitatively interpreted by assuming the ratios of apparent cross sections as follows;

$$\text{Cl 2s/C 1s} = 1.14$$
$$\text{Cl 2p/C 1s} = 2.02$$

The observed spectra of valence-electron region are shown in Figs. 3 and 4, where the observed data are shown by points, the solid lines being the calculated spectra which will be discussed later. The spectra of chloromethanes are very similar to each other. The same can be said also for the spectra of chloroethanes. We can roughly divide each spectrum into three parts; (1) The most intense peak at about 12 eV, which seems to be predominantly associated with Cl 3p lone pairs, (2) the peaks in the region of 15—22 eV, which are likely to be due to the orbitals associated with chemical bonds, and (3) the very broad bands with long tails in the region of 22—35 eV, where the peaks seem to be attributable to the molecular orbitals mainly associated with Cl 3s and C 2s atomic orbitals, possibly the long tails being due to shake-up or shake-off processes.

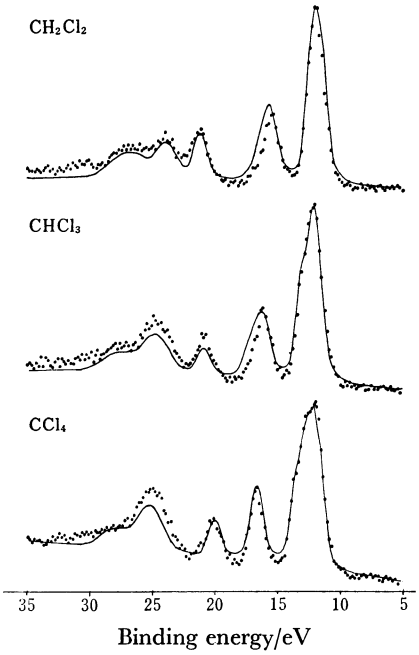


Fig. 3. Valence electron spectra of chloromethanes. Solid lines are the calculated spectra.

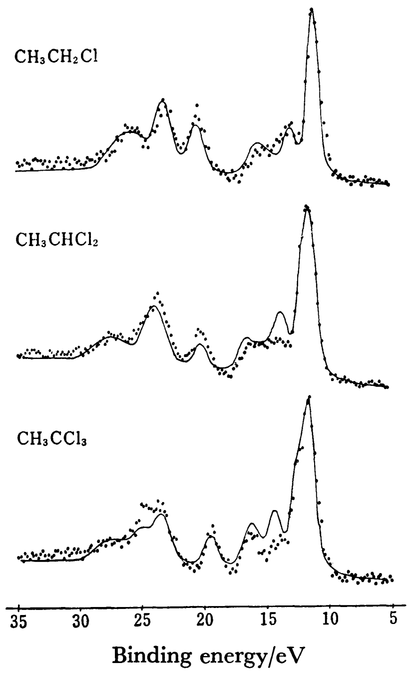


Fig. 4. Valence electron spectra of chloroethanes. Solid lines denote the calculated spectra.

Discussion

Binding Energies of Core-electron Levels. According to the electrostatic potential model, developed by Siegbahn and his co-workers,[10] core-electron binding energies can be correlated with charge distribution in molecule by the following relation;

$$E_i = E_0 + kq_i + \sum_{j\neq i}(q_j/R_{ij}) \qquad (1)$$

where E_i is the binding energy of a core-electron level of the atom i,q_j is the charge on the atom j, R_{ij} is the interatomic distance, and k is a constant characteristic of the kind of atom. In this equation, the second term gives the energy shift due to the charge on the atom i, and the third one is the contribution of the electrostatic potential due to surrounding atoms. This electrostatic potential model has been successfully used in conjunction with the charge density calculated by the CNDO/2 method.

Although the CNDO/2 method is widely used for a variety of organic molecules, the procedures of treating chlorine-containing molecules by the CNDO/2 method has not yet wholly established. There remains a problem concerned with the suitable extent of including vacant 3d atomic orbitals of chlorine in the CNDO/2 calculation of chlorine-containing molecules. In the present study, we carried out calculations by the two extreme methods; Method (a) is that proposed by Santry and Segal,[12] where the 3d orbitals of chlorine are included in the basis set, assuming their orbital exponents the same as those of the 3s and 3p atomic orbitals of chlorine, and Method (b) is the one which completely neglects the 3d orbitals of chlorine. The charge densities obtained by the above two methods are compared in Table 2. It should be noted that there is a significant difference between the charge distributions predicted by these two methods.

According to Eq. 1, we shall obtain a straight line when we plot $E_i - \sum_{i\neq j}(q_j/R_{ij})$ against q_i for a given kind of core-electron level, for example, for C 1s levels. The inclination of the line corresponds to the constant k and its intercept at $q_i=0$ gives the E_0 value. In Fig. 5, we have plotted $E_i(\text{obsd}) - \sum_{i\neq j}(q_j/R_{ij})$ against q_i, using the

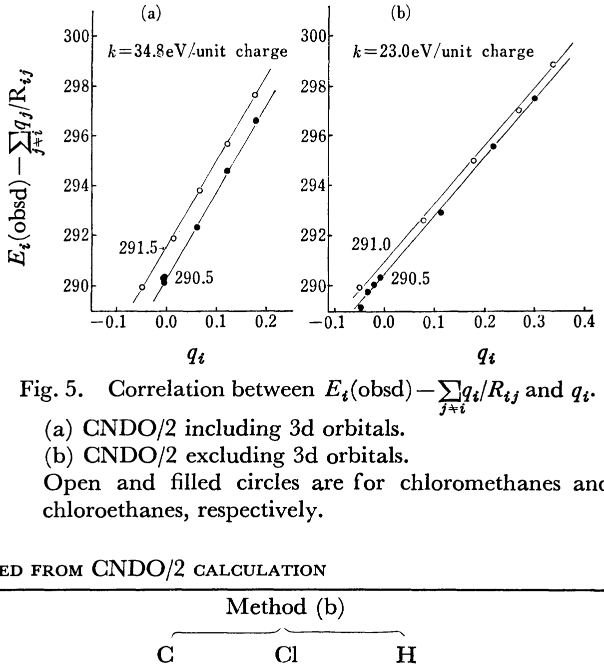


Fig. 5. Correlation between $E_i(\text{obsd}) - \sum_{j\neq i} q_i/R_{ij}$ and q_i.
(a) CNDO/2 including 3d orbitals.
(b) CNDO/2 excluding 3d orbitals.
Open and filled circles are for chloromethanes and chloroethanes, respectively.

Table 2. Charge densities obtained from CNDO/2 calculation

	Method (a)			Method (b)		
	C	Cl	H	C	Cl	H
CH_4	−0.050		0.012	−0.050		0.012
CH_3Cl	0.0125	−0.1233	0.0369	0.0756	−0.1288	0.0177
CH_2Cl_2	0.0633	−0.0905	0.0589	0.1765	−0.1107	0.0225
$CHCl_3$	0.1198	−0.0645	0.0738	0.2647	−0.0959	0.0231
CCl_4	0.1770	−0.0443		0.3367	−0.0842	

	Method (a)				Method (b)			
	C_a	C_b	Cl	H	C_a	C_b	Cl	H
CH_3CH_3	−0.09	−0.09		0.03	−0.09	−0.09		0.03
CH_3CH_2Cl	0.0595	−0.0055	−0.1452	0.0140	0.1143	−0.0237	−0.1513	0.0121
CH_3CHCl_2	0.1194	−0.0040	−0.1144	0.0233	0.2150	−0.0374	−0.1355	0.0233
CH_3CCl_3	0.1778	−0.0019	−0.0891	0.0305	0.3006	−0.0474	−0.1213	0.0369

observed binding energies of C 1s levels and calculated charge densities. The plots fall on a straight line for the charge densities obtained by Method (a) as well as for those by Method (b), but the inclination of line significantly differs between the two cases, giving the following k values, respectively;

$$\text{Method (a)};\ k(\text{C 1s}) = 34.8\ \text{eV}/\textit{unit charge}$$

$$\text{Method (b)};\ k(\text{C 1s}) = 23.0\ \text{eV}/\textit{unit charge}$$

In our previous paper, we obtained 22.67 eV/*unit charge* for k(C 1s) from the analysis of observed C 1s binding energies of benzene derivatives using CNDO/2 charge densities.[1)] The k value of 23.0 eV/*unit charge* obtained here for the charge densities by the calculations with Method (b), is in good agreement with the above result, but the k value of 34.8 eV/*unit charge*, which was obtained for the charge densities calculated by Method (a), seems to be too large. The same conclusion has been derived recently by Clark *et al.*[13)] from the study of XPS spectra of chlorobenzenes in solid phase. The equation of electrostatic potential model, (Eq. 1), can be reinterpreted quantum-mechanically for CNDO scheme.[14)] According to this interpretation, the constant k corresponds to the Coulomb repulsion potential between a core electron and an electron in the valence shell, so that it can be theoretically calculated. When such a calculation is done for carbon atom by use of Slater AO's, we obtain 22.0 eV/*unit charge* for k(C 1s), which is close to the k value obtained here for the charge densities calculated by Method (b). However it should be noted that the point charge approximation, on which Siegbahn's electrostatic potential model has been derived, has a serious problem in the case of molecules which contain large atoms such as chlorine, because there can be a relatively large contribution of polarization in the electrostatic potential. At the same time, we have to consider that relaxation energy may appreciably increase by replacing hydrogen with chlorine.[15)] Both of these effects are expected to reduce the apparent k value. In other words, the k value experimentally determined by the electrostatic potential model must be smaller than the theoretical value if the above effects are significant. When this situation is taken into account, the k value of 23.0 eV/*unit charge* seems to be already a little too large, and the k value of 34.8 eV/*unit charge* is apparently unreasonable. Therefore, we can conclude that Method (b), which neglects 3d orbitals of chlorine, gives better results than Method (a), at least for charge densities.

It should be noted in Fig. 5 that the plots for chloromethanes and those for chloroethanes are on separate lines with the same inclination. From the intercepts of these lines at $q_i=0$ in Fig. 5 (b), we obtain the following values for E_0 (C1s);

$$E_0(\text{C 1s}) = 291.0\ \text{eV} \quad \text{for chloromethanes}$$

$$E_0(\text{C 1s}) = 290.5\ \text{eV} \quad \text{for chloroethanes}$$

It is noteworthy that almost the same values are obtainable from Fig. 5 (a) which has used the charge densities calculated by Method (a).

We have previously obtained 290.2 eV for E_0(C 1s) in the case of benzene derivatives.[1)] As compared with this value, the E_0 value for chloromethanes is larger by 0.8 eV and that for chloromethanes is larger by 0.3 eV. Presumably, the above differences of E_0 values reflect the differences concerned with relaxation energy.

The binding energies of Cl 2s and Cl 2p levels slightly increase with the number of chlorine atoms. This change corresponds qualitatively to the decrease of the negative charges on chlorine atoms. However, the number of available data is so limited that it is not possible in these cases to quantify the correlation between binding energy and charge density.

Analysis of Valence-electron Spectra. The photoionization cross section of a molecular orbital is approximately given by the overlap integral between the molecular orbital and the photoelectron final-state wave function which can be expressed as a plane wave orthogonalized to the initial state. In the case of XPS, this overlap integral is almost entirely determined by the contributions from the parts very close to the nuclei, because of the short de Broglie wavelength of photoelectron. On the basis of this idea, Gelius[16)] proposed that the molecular orbital cross section may be expressed as a sum over contributions from each atomic centers, as follows;

$$\sigma_j \propto (2+\beta/2)\sum_{\mathrm{A}\lambda} P_{\mathrm{A}\lambda}^{(j)}\sigma_{\mathrm{A}\lambda} \tag{2}$$

where $P_{\mathrm{A}\lambda}^{(j)}$ denotes the probability of finding the electron in the j-th molecular orbital in an atomic orbital $A\lambda$, $\sigma_{\mathrm{A}\lambda}$ is the cross section of the atomic orbital $A\lambda$, and β is the asymmetry parameter, $-1 \leqq \beta \leqq 2$. In the case of chloromethanes and chloroethanes, one may use an average value of β instead of the true asymmetric parameters without significant influence on the calculated intensities. Thus, using relative atomic cross section $\sigma(A\lambda/\mathrm{C2s})=\sigma_{\mathrm{A}\lambda}/\sigma_{\mathrm{C2S}}$, we can express the intensity of the peak associated with the photoionization of the j-th molecular orbital, as follows;

$$I_j \propto \sum_{\mathrm{A}\lambda} P_{\mathrm{A}\lambda}^{(j)}\sigma(\mathrm{A}\lambda/\mathrm{C\ 2s}) \tag{3}$$

The simulation of valence-electron spectra, by use of the above intensity model, is useful for the analysis of valence-electron spectra.[16—20)] In the present study, we carried out spectrum simulation adopting the following procedures:

(1) $P_{\mathrm{A}\lambda}^{(j)}$ was calculated by CNDO/2 with neglect of 3d orbitals of chlorine (Method (b)). Incidentally, the CNDO/2 calculations including 3d orbitals of chlorine (Method (a)) gave the values of $P_{\mathrm{A}\lambda}^{(j)}$ which are not significantly different from those obtained by Method (b).

(2) The shape of each photoelectron peak was assumed to be the one that is expressed by the modified Lorentzian function (Eq. 4).

$$f_j(\chi) = 0.5I_j\left\{\frac{1}{1+\left(\frac{2\chi}{w_j}\right)^2}+\frac{1}{1+\left(\frac{2\chi}{w_j}\right)^4}\right\} \tag{4}$$

where χ is the energy measured from the center of the peak and w_j is the half-width. The value of w_j was fixed as 1.1 eV for peaks in the Cl 3p lone-pair region, and as 1.3 eV for those in the chemical-bonding region, but it was treated as an adjustable parameter for peaks in the Cl 3s region.

(3) The order of valence-electron levels was assumed the same as that predicted by the CNDO/2 calculation

Table 3. Calculated and experimental valence orbitals of chloromethanes

Molecule	Symmetry	CNDO/2 calculation						IP (obsd) (eV)		Peak width (eV)
		atomic population				Orbital energy (eV)	Relative cross section	UPS[a)]	XPS	
		C 2s	C 2p	Cl 3s	Cl 3p					
CH_2Cl_2	$3b_2$	—	0.051	0.000	0.948	−14.09	0.95	11.40	11.4	1.1
	$2b_1$	—	0.046	—	0.840	−14.42	0.84			
	$4a_1$	0.001	0.075	0.000	0.874	−14.57	0.88	12.22	12.2	1.1
	$1a_2$	—	—	—	1.000	−15.17	1.00			
	$2b_2$	—	0.273	0.052	0.676	−17.66	0.75	15.30	15.3	1.3
	$3a_1$	0.024	0.247	0.078	0.612	−19.05	0.76	15.94	15.9	1.3
	$1b_1$	—	0.455	—	0.152	−22.94	0.19	16.77	16.8	1.3
	$2a_1$	0.099	0.133	0.542	0.040	−26.76	0.79	(20.3)	21.1	1.3
	$1b_2$	—	0.095	0.898	0.006	−29.28	0.91		23.9	2.0
	$1a_1$	0.411	0.000	0.334	0.058	−36.95	1.21		27.0	3.5
$CHCl_3$	$4a_1$	0.000	0.071	0.000	0.821	−14.49	0.83	11.48	11.5	1.1
	$1a_2$	—	—	—	1.000	−14.75	1.00	11.91	12.0	1.1
	4e	—	0.080	0.000	0.920	−14.14	2.37	12.01		
	3e	—	0.011	0.000	0.989	−15.72	1.98	12.85	12.9	1.1
	2e	—	0.230	0.074	0.622	−19.05	1.43	15.99	16.0	1.3
	$3a_1$	0.067	0.204	0.150	0.533	−20.87	1.67	16.96	17.0	1.3
	$2a_1$	0.102	0.201	0.354	0.100	−26.10	0.68	(19.8)	20.8	1.3
	1e	—	0.104	0.876	0.020	−29.79	1.81		24.6	2.5
	$1a_1$	0.372	0.000	0.453	0.083	−37.57	1.28		27.5	3.5
CCl_4	$1t_1$	—	—	—	1.000	−15.01	1.50	11.69	11.7	1.1
	$3t_2$	—	0.098	0.000	0.902	−14.14	1.37	12.44	12.5	1.1
	1e	—	—	—	1.000	−16.56	1.00	13.37	13.4	1.1
	$2t_2$	—	0.215	0.098	0.687	−20.03	1.21	16.58	16.6	1.3
	$2a_1$	0.214	—	0.404	0.382	−22.86	0.61	(20.0)	20.0	1.3
	$1t_2$	—	0.113	0.854	0.033	−30.25	1.35		24.8	2.4
	$1a_1$	0.337	—	0.552	0.111	−38.08	0.67		28.0	3.0

a) Ref. 4 Potts *et al.* Ionization potentials obtained with He II radiation are given in parentheses.

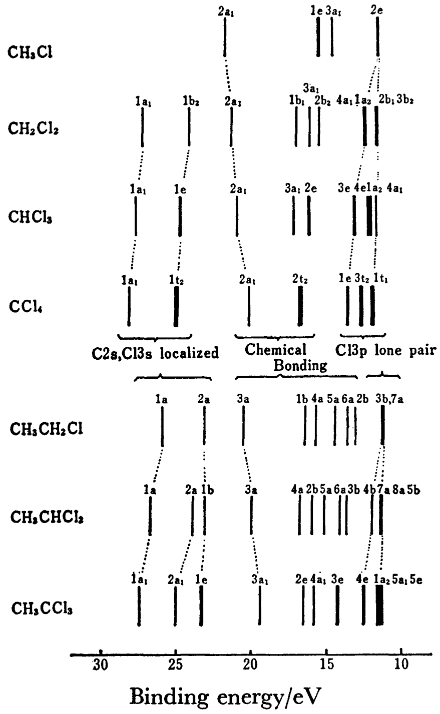


Fig. 6. Correlation diagram of observed valence electron energies for chloromethanes and chloroethanes.

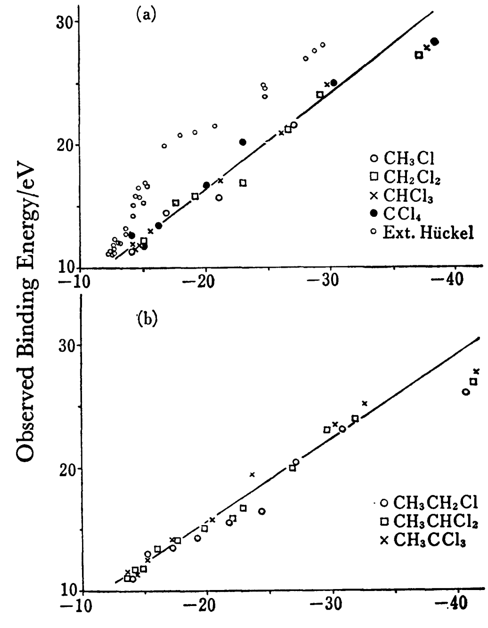


Fig. 7. Relation between observed ionization energies and CNDO/2 orbital energies.

(a) Chloromethanes, (b) chloroethanes.

Data obtained with extended Hückel type calculation by Hopfgarten and Manne are shown as small open circles in (a).

TABLE 4. CALCULATED AND EXPERIMENTAL VALENCE ORBITALS OF CHLOROETHANES

Molecule	Symmetry	CNDO/2 calculation						*IP*(obsd) (eV)		Peak width (eV)
		Atomic population				Orbital energy (eV)	Relative cross section	UPS[a]	XPS	
		C 2s	C 2p	Cl 3s	Cl 3p					
CH_3CH_2Cl	7a	0.005	0.093	0.000	0.874	−13.98	1.00	11.06	11.1	1.1
	3b	—	0.046	—	0.842	−14.04	0.95			
	6a	0.003	0.307	0.010	0.476	−15.27	0.58	13.01	13.0	1.3
	2b	—	0.375	—	0.116	−17.32	0.17	13.51	13.5	1.3
	5a	0.000	0.675	0.014	0.131	−19.13	0.23	14.35	14.6	1.3
	4a	0.024	0.455	0.127	0.118	−21.81	0.37	15.60	15.6	1.3
	1b	—	0.563	—	0.037	−24.47	0.10	16.35	16.4	1.3
	3a	0.123	0.242	0.368	0.010	−27.28	0.72		20.4	1.5
	2a	0.255	0.124	0.373	0.016	−30.80	1.02		23.0	1.5
	1a	0.616	0.048	0.060	0.018	−40.78	1.47		25.8	3.5
CH_3CHCl_2	5b	—	0.073	0.000	0.913	−13.73	1.00	11.23	11.2	1.1
	8a	0.008	0.133	0.000	0.816	−14.09	0.92			
	7a	0.001	0.104	0.000	0.795	−14.27	0.88	11.92	11.9	1.1
	4b	—	0.014	0.000	0.965	−14.85	0.87			
	3b	—	0.229	0.010	0.628	−15.99	0.72	13.61	13.6	1.3
	6a	0.004	0.261	0.013	0.468	−17.42	0.56	14.03	14.0	1.3
	5a	0.005	0.536	0.042	0.250	−19.77	0.38	15.12	15.1	1.3
	2b	—	0.428	0.142	0.125	−22.00	0.33	15.93	15.9	1.3
	4a	0.072	0.417	0.171	0.146	−22.76	0.54	16.74	16.7	1.3
	3a	0.098	0.347	0.206	0.044	−26.77	0.52		19.9	1.3
	1b	—	0.164	0.800	0.012	−29.62	0.90		23.0	1.5
	2a	0.251	0.120	0.406	0.031	−31.81	1.03		23.8	1.5
	1a	0.598	0.049	0.117	0.036	−41.25	1.47		26.6	3.5
CH_3CCl_3	$5a_1$	0.11	0.178	0.000	0.880	−14.18	0.92	11.25	11.3	1.1
	5e	—	0.100	0.000	0.804	−13.82	1.63	11.58	11.6	1.1
	$1a_2$	—	—	0.000	1.000	−14.53	1.00			
	4e	—	0.037	0.000	0.924	−15.28	1.85	12.50	12.5	1.1
	3e	—	0.195	0.013	0.657	−17.32	1.37	14.24	14.2	1.3
	$4a_1$	0.026	0.354	0.091	0.494	−20.17	0.67	15.76	15.8	1.3
	2e	—	0.408	0.166	0.152	−22.49	0.71	16.44	16.4	1.3
	$3a_1$	0.182	0.289	0.275	0.144	−23.76	0.81		19.4	1.3
	1e	—	0.176	0.775	0.025	−30.19	1.63		23.3	1.5
	$2a_1$	0.250	0.119	0.420	0.044	−32.60	0.97		25.0	1.5
	$1a_1$	0.598	0.050	0.171	0.037	−41.60	1.41		27.4	3.0

a) Ref. 7.

with a few exceptions.[21] For the orbitals within reach of UPS, we used the binding energies reported by Pott *et al.*[4] for chloromethanes, and by Katsumata and Kimura[7] for chloroethanes. For the peaks at binding energies above 17 eV, we adjusted peak positions so as to give the best agreement between calculated and observed spectra.

In order to calculate the valence-electron spectra of chloromethanes and chloroethanes, we need to know three relative atomic cross sections, σ(C 2p/C 2s), σ(Cl 3s/C 2s) and σ(Cl 3p/C 2s), parametrized for CNDO/2 orbitals.[22] Banna *et al.*[20] has determined σ(C 2p/C 2s) from the analysis of the XPS spectrum of methane using CNDO/2 orbitals. Since the remaining two relative cross sections have not been known, we treat them as parameters, and found that the following values give the best over-all agreement between calculated and observed spectra for all chloromethanes and chloroethanes;[23]

$$\sigma(\mathrm{Cl\ 3s/C\ 2s}) = 0.50$$

$$\sigma(\mathrm{Cl\ 3p/C\ 2s}) = 0.50$$

The final results of spectrum simulation are shown by solid lines in Figs. 3 and 4 for chloromethanes and chloroethanes, respectively. The agreement with observed spectrum is very satisfactory in every case.

The binding energies and half-widths of photoelectron peaks finally employed in the above simulations are listed in Tables 3 and 4, together with the results of CNDO/2 calculations. It should be noted that the peaks at binding energies of 22—35 eV are very much broadened, having a width of 2.5—3.5 eV. These peaks are due to the molecular orbitals mainly associated with Cl 3s and C 2s atomic orbitals. Seemingly, the above phenomena are due to the life-time broadening, since a hole in these molecular orbitals is expected to decay rapidly by the Coster-Kronig process.

The photoelectron bands of chloromethanes at binding energies of about 20 eV were also studied by Potts *et al.* by means of UPS with He II resonance line.[4] The binding energies reported by them are considerably different from our values, the discrepancies being as large as 1 eV. However, very recently, Katsumata and Kimura[24] carefully measured the UPS spectra of chloromethanes employing the He II line, and obtained the values which agree well with our XPS data.

Figure 6 shows the correlation diagram of valence electron levels of chloromethanes and chloroethanes. By examining the atomic populations, given in Tables 3 and 4, molecular orbitals can be roughly divided into three groups; (1) Cl 3p lone-pair orbitals (2) chemical-bonding orbitals, and (3) orbitals predominantly associated with Cl 3s and C2s. As it is naturally expected, Cl 3p lone-pair levels split wider on increasing the number of chlorine atoms in the case of chloromethanes as well as in the case of chloroethanes. The main features of this splitting are nearly the same between the two cases.

In Fig. 7, we have plotted the observed binding energies against the corresponding orbital energies obtained by CNDO/2 calculations. Most of the plots are on a straight line for each series of compounds, so that we can derive the following empirical relations between binding energy E_B and CNDO/2 orbital energy $\varepsilon_{\mathrm{CNDO/2}}$; For chloromethanes,

$$E_B = 0.78(-\varepsilon_{\mathrm{CNDO/2}}-2.9)\ \mathrm{eV},$$

and, for chloroethanes,

$$E_B = 0.72(-\varepsilon_{\mathrm{CNDO/2}}-2.9)\ \mathrm{eV}.$$

Extended Hückel type (EHT) calculation is often used in the analysis of photoelectron spectrum. In Fig. 7(a), we have also plotted the observed binding energies against the orbital energies obtained with EHT calculation.[25] It should be noted that orbital energies by EHT calculations do not show such a simple correlation with observed binding energies as we have obtained for CNDO/2 orbital energies.

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21) There are some ambiguities in the assignment of MO's in the Cl 3p region. Although several possible cases were tried in the course of spectra simulation, we could not find a clear difference in these simulated curves. Accordingly, we have adopted the same assignment as those proposed by Hopfgarten and Manne (Ref. 25) for chloromethanes.

As for 1,1,1-trichloroethane, it would be reasonable to assign the first ionization potential to 5*a*, instead of 5*e* from the consideration of UPS spectral intensity. This assignment is contradicted with the CNDO/2 result.

22) As the cross section of H ls is much smaller than those of C 2s, 2p, Cl 3s, 3p in the XPS region, the contribution of H ls was neglected in the spectral simulation. (See for example, V. I. Nefedov *et al.*, *J. Electron Spectrosc.*, **2**, 383 (1973).

23) Most recently Berndtsson *et al.* (*Physica Scripta*, **12**, 235 (1975)) has measured XPS valence electron spectra of chloroethylenes and performed the spectral simulation by using extended Hückel type MO's. They determined the experimental relative cross sections for Cl 3s and Cl 3p, as follows,

$$\sigma(\mathrm{Cl\ 3s/C\ 2s}) = 0.69$$

$$\sigma(\mathrm{Cl\ 3p/C\ 2s}) = 0.58$$

These values are slightly higher than ours.

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