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Photoelectron Spectra and Orbital Structures of Higher Alkyl Chlorides, Bromides, and Iodides

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High-resolution photoelectron spectra of alkyl halides RX (R=ethyl, *n*-propyl, and *n*-butyl; X=Cl, Br, and I) were measured with the 584 Å line of helium. In the region below about 17 eV, six bands were observed for each of the ethyl halides, eight bands for each of the *n*-propyl halides, and ten bands for each of the *n*-butyl halides. All the observed vertical ionization energies were plotted against Pauling's electronegativity of the halogen atom, indicating that there are approximate linear relationships. Assuming Koopmans' theorem, total and partial sums of experimental orbital energies were calculated using the observed ionization energies for the individual alkyl halides and found to be well reproduced by calculating the sums of empirical orbital-energy values for several localized orbitals such as n(X), n'(X), σ(C–X), σ(C–C), $\pi(CH_3)$, $\pi'(CH_3)$, and $\pi(CH_2)$. From a comparison of the experimental and calculated partial orbital-energy sums, assignments of the photoelectron bands to the localized molecular orbitals were made for each of the alkyl halides.

It is known in photoelectron spectroscopy that removal of a lone-pair electron gives rise to the first ionization with a sharp band distinguishable from other types of electrons such as π and σ electrons. As a result, the ionization energies of the lone pair electrons can be accurately determined, thus attracting attention to the photoelectron spectra of various compounds containing halogen atoms.

With respect to alkyl halides, several photoelectron studies[1-6,8] have been carried out with high-resolution photoelectron technique during the last few years. Turner[1] first succeeded in measuring high-resolution photoelectron spectra for many compounds including some halogen-containing compounds. Ragle

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[1] D. W. Turner, "Molecular Photoelectron Spectroscopy," John Wiley & Sons, New York, N. Y. (1969).

[2] J. L. Ragle, I. A. Stenhouse, D. C. Frost, and C. A. McDowell, *J. Chem. Phys.*, **53**, 178 (1970).

[3] A. W. Potts, H. J. Lempka, D. G. Streets, and W. C. Price, *Phil. Trans. Roy. Soc. Lond.*, **A**, **268**, 58 (1970).

[4] J. A. Hashmall and E. Heilbronner, *Angew. Chem. Internat. Edit.*, **9**, 305 (1970).

[5] A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Anal. Chem.*, **43**, 375 (1971).

[6] F. Brolgi and E. Heilbronner, *Helv. Chim. Acta*, **54**, 1424 (1971).

[7] R. N. Dixon, J. N. Murrell, and B. Narayan, *Molecular Phys.*, **20**, 611 (1971).

[8] A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Int. J. Mass Spectrum Ion Phys.*, **4**, 90 (1970).

et al.[2] reported on the photoelectron spectra of many halomethanes including methyl halides and interpreted each of the observed bands in terms of molecular orbital structure from a comparative study of the spectra. For a series of alkyl bromides, Hashmall and Heilbronner[4] reported an interesting comparison of their first ionization energies obtained from the high-resolution photoelectron spectra, and concluded that the first ionization energy is reduced by 0.2 eV by methyl substitution on the α-position and by 0.09 eV on the β-position.

Photoelectron spectra of methyl iodide and several alkyl iodides have been studied by Baker *et al.*[5] together with other halogen-containing compounds from an analytical point of view, indicating that there is a correlation between the first ionization energies and the Taft σ values of the alkyl groups.

The "lone pair" bands of the series of the alkyl iodides as well as alkyl bromides have been studied theoretically in detail by Brogli and Heilbronner[6] in terms of the spin-orbit coupling. The photoelectron bands associated with ionization from the formally non-bonding p orbitals of the halogen atoms in various halomethanes have been interpreted by Dixon *et al.*,[7] in terms of a pseudo one-electron hamiltonian.

Photoelectron data of *n*-butyl iodide except for the first-ionization band has not so far been found in literature. Several photoelectron studies of alkyl halides mentioned above are available, but no systematic and comparative photoelectron studies covering higher alkyl chlorides, bromides and iodides have been published yet.

We have carried out a systematic and comparative study of not only the first but also the higher ionization energies of ethyl, *n*-propyl and *n*-butyl halides by means of a high-resolution photoelectron technique, with the aim first to deduce some correlations of ionization energies of alkyl halides with carbon chain and electronegativity of the halogen atom, and secondly to clarify valence orbital structures of the series of normal alkyl halides up to the butyl halides.

Experimental

Commercial alkyl halides were used after purification. Measurements of photoelectron spectra were carried out with a JASCO PE-1 high-resolution photoelectron spectrometer, containing an electrostatic semispherical analyzer, using helium 584 Å (21.22 eV) resonance line. Detection of photoelectrons was made with an electron multiplier coupled to an amplifier, discriminater and rate meter. The typical working resolution of this spectrometer was 20—25 meV. Calibration of an ionization-energy scale from the analyzer voltage was carried out using known ionization energy values of Ar and Xe as standard substances.

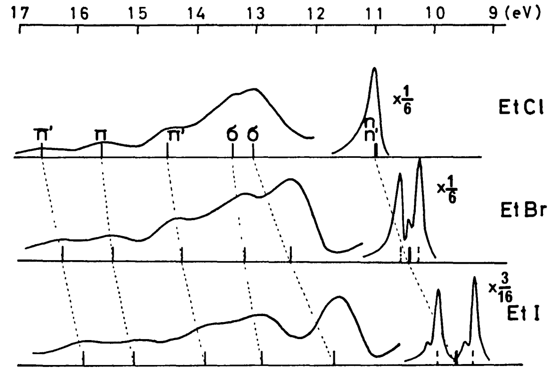

Fig. 1. Photoelectron spectra of ethyl halides.

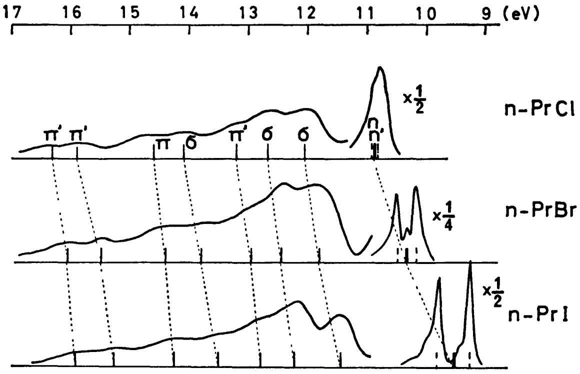

Fig. 2. Photoelectron spectra of *n*-propyl halides.

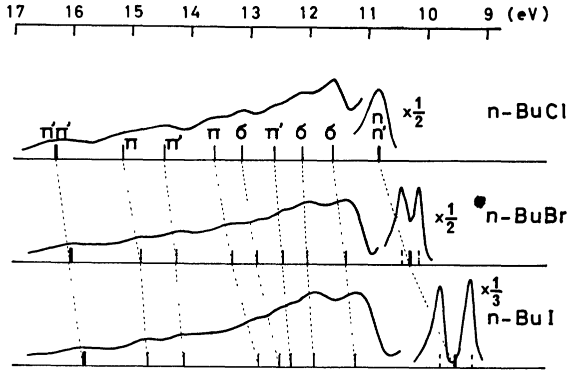

Fig. 3. Photoelectron spectra of *n*-butyl halides.

Results and Discussion

Photoelectron Spectra and Ionization Energies. Observed photoelectron spectra for ethyl, *n*-propyl and *n*-butyl halides (X=Cl, Br, and I) are shown in Figs. 1—3. General aspects of these spectra differ from those of the corresponding methyl halides except for the first bands, the spectrum becoming successively complicated as the alkyl group is ascended.

A comparative and systematic study is of merit for determining ionization energies from the photoelectron spectra.

First a brief review of the spectral features of methyl halides (CH_3X)[2,3] will provide a basis for interpreting electronic structures and photoelectron spectra of higher alkyl halides. In the methyl halides four photoelectron bands ascribed to different orbitals have been observed below *ca.* 22 eV. The first bands accompany spin-orbit splittings and vibrational structures are assigned to ionization of the non-bonding orbitals. The second bands ascribed to the C–X bonding orbitals show relatively broad maxima without any structure, and the third bands due to the pseudo

π orbitals of CH_3 are composed of double maxima due to the Jahn-Teller splitting. The fourth band appearing at *ca.* 20 eV has tentatively been assigned to the C 2s orbital.[3]

Spectral features observed for the higher alkyl halides are as follows.

Ethyl Halides. As seen from Fig. 1, a total of six bands appear for the individual ethyl halides, the first bands with structures very similar in spectral shape to those of the corresponding methyl halides. A slight shoulder appearing on high energy side of the second band of ethyl chloride is considered to be an independent band corresponding to the third inner orbital. Mean vertical ionization energies obtained from the maxima or shoulders of their photoelectron spectra are summarized in Table 1, the values obtained from the shoulders being shown in parentheses.

TABLE 1. VERTICAL IONIZATION ENERGIES OF ETHYL HALIDES (IN eV)

	This work			Other works		
	EtCl	EtBr	EtI	EtBr[4]	EtI[5]	EtI[6]
$I_1(^2E_{3/2})$		10.28	9.34	10.30	9.37	9.35
$I_1(^2E_{1/2})$		10.60	9.93	10.61	9.93	9.93
$(I_1)_{av}$	11.01	10.44	9.63_5	10.45_5	9.65	9.64
I_2	13.07	12.44	11.66		11.68	
I_3	(13.4)	13.20	12.90		12.90	
I_4	14.50	14.25	13.85		13.80	
I_5	15.60	15.40	15.05		15.00	
I_6	16.60	16.25	15.90		15.90	

In order to find some correlation among the ethyl-halide data, we plotted the observed ionization energies against Pauling's electronegativities of the halogen atoms (Fig. 4) in which six kinds of observed ionization energies correspond well to each other. Such correlation diagrams are also drawn for other series of the alkyl halides in Fig. 4. In Fig. 5, the first and second ionization-energy plots of the ethyl halides are compared with those of the other higher halides.

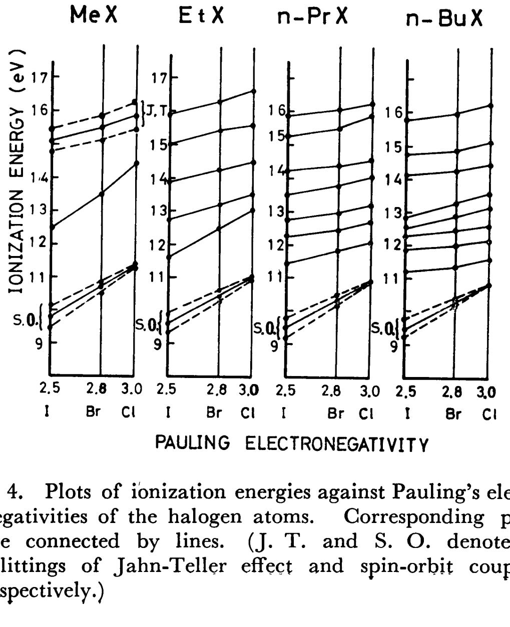

Fig. 4. Plots of ionization energies against Pauling's electronegativities of the halogen atoms. Corresponding points are connected by lines. (J. T. and S. O. denote the splittings of Jahn-Teller effect and spin-orbit coupling, respectively.)

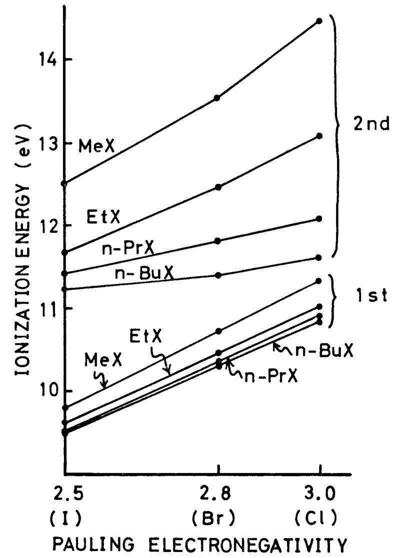

Fig. 5. Comparison of the first and second ionization-energy plots for the alkyl halides.

n-Propyl Halides. The photoelectron spectra of the series of the *n*-propyl halides are compared in Fig. 2. For these compounds a total of eight bands are distinguishable from the overall spectra. The resulting ionization energies are summarized in Table 2. Here also slight shoulders appear at *ca.* 13.2 eV for *n*-PrCl and *ca.* 12.9 and 13.8 eV for *n*-PrBr.

TABLE 2. VERTICAL IONIZATION ENERGIES OF *n*-PROPYL HALIDES (IN eV)

	This work			Other works		
	n-PrCl	*n*-PrBr	*n*-PrI	*n*-PrBr[4]	*n*-PrI[5]	*n*-PrI[6]
$I_1(^2E_{3/2})$		10.18	9.27	10.18	9.27	9.25
$I_1(^2E_{1/2})$		10.50	9.82	10.49	9.84	9.83
$(I_1)_{av}$	10.88	10.34	9.53_5	10.33_5	9.55_5	9.54
I_2	12.06	11.81	11.43		11.46	
I_3	12.68	12.45	12.22		12.25	
I_4	(13.2)	(12.9_5)	12.78		12.80	
I_5	14.10	(13.8)	(13.5)			
I_6	14.60	14.40	14.25		14.25	
I_7	15.90	15.50	15.25		15.30	
I_8	16.30	16.05	15.90		15.95	

Seven ionization energy values have already been reported for *n*-PrI by Baker *et al.*,[5] whereas we identified a total of eight bands including the 13.5 eV band which appears as only a slight shelf. Good correlations were obtained for the observed ionization energies among the *n*-propyl halides as in the case of the ethyl halide series.

n-Butyl Halides. In the *n*-butyl halides the situation is much more complicated with overlapping bands in the photoelectron spectra. However, we can identify a total of at least ten bands from the observed spectra of the *n*-butyl halides by the aid of the correlation diagram (Fig. 4). The resulting values are given in Table 3.

Some literature values, though incomplete, are available for comparison with the present data, as

TABLE 3. VERTICAL IONIZATION ENERGIES OF *n*-BUTYL HALIDES (IN eV)

	This work			Other works	
	n-BuCl	*n*-BuBr	*n*-BuI	*n*-BuBr[4)]	*n*-BuI[6)]
$I_1(^2E_{3/2})$		10.15	9.24	10.13	9.23
$I_1(^2E_{1/2})$		10.44	9.79	10.44	9.81
$(I_1)_{\mathrm{av}}$	10.84	10.29_5	9.51_5	10.28_5	9.52
I_2	11.61	11.38	11.22		
I_3	12.13	12.03	11.90		
I_4	(12.6)	12.45	(12.3)		
I_5	13.14	(12.9)	12.50		
I_6	13.60	13.30	(12.8_5)		
I_7	14.45	14.25	(14.1)		
I_8	(15.1_5)	14.85	14.70		
I_9 I_{10}	16.25	16.00	15.75		

shown in Tables 1—3. For the alkyl chlorides except methyl chloride, no photoelectron data are available for comparison. For a series of alkyl bromides, no higher ionization energies have been reported previously. The first ionization energies including spin-orbit splittings reported by Hashmall and Heilbronner[4)] were essentially in agreement with our corresponding data. Furthermore, in alkyl iodides, ethyl, *n*-propyl and *n*-pentyl iodides have been studied by photoelectron spectroscopy by Baker *et al.*,[5)] but *n*-butyl iodide has not been included. As far as comparison is possible, excellent agreements were obtained.

Alkyl Substituent Effect on First Ionization. In Fig. 6, variations in the first mean ionization energies are shown for the alkyl halides from the methyl to *n*-butyl halides. Their higher normal homologues can be expected to tend to converge to nearly constant values.

It has been pointed out that the mean first ionization energies of the alkyl bromides are reduced by 0.2 eV per α-methyl substituent and by 0.09 eV per β-methyl substituent.[4)] It is interesting to note that in the series of the alkyl chlorides, bromides and iodides, the ionization energy variation due to the methyl substitution on γ-position still amounts to as much as 0.02—0.05 eV.

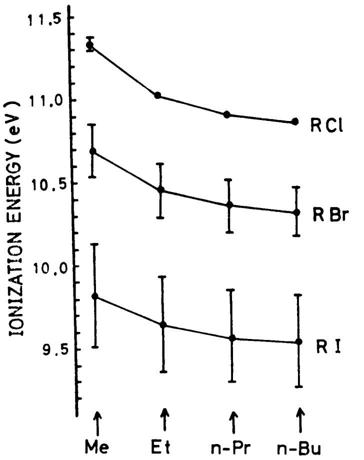

Fig. 6. The effect of carbon chain on the mean first ionization energies for the alkyl chlorides, bromides and iodides. Magnitudes of the spin-orbit splittings are also shown.

Correlation with Pauling's Electronegativity of Halogen Atom. It is interesting to examine how halogen atoms depend on ionization energies. The available ionization energies for the methyl halides are plotted for comparison (Figs. 4—6). As seen from Fig. 5, there are more or less linear relationships for many sets of ionization energy. Baker *et al.*[8)] have pointed out that such a linear relationship is found for the first ionization energies of methyl halides. A similar correlation has now been found for the higher alkyl halides.

The gradient of the lines plotted in the correlation diagram is considered to express a measure of contribution from the halogen atoms. It is expected that the greater the contribution of the halogen atom, the steeper the line.

Let us consider the first ionization of the series of alkyl halides. The lowest straight lines corresponding to the first ionization show almost parallel relationships but become slightly less steep as the series ascends. The gradient of these lines may roughly be related to the magnitude of contribution of halogen p orbital by the following consideration. Assuming Koopmans' theorem, the lone-pair orbital ε_1 can be given by

$$\varepsilon_1 = c_x{}^2F_{xx} + \sum_{\nu} c_{1x}c_{1\nu}F_{x\nu} + \cdots \tag{1}$$

where F_{xx} is a Hamiltonian element expressed in terms of the halogen p atomic orbitals. Since the molecular orbitals associated with the first ionization are expected to be largely contributed by the halogen p orbitals, coefficient c_x in the first term should be predominantly large. In the CNDO/2 approximation,[9)] F_{xx} can be expressed by

$$F_{xx} = -\frac{1}{2}(I_x+A_x) + \cdots \tag{2}$$

It should be noticed that the first term in Eq. 2 is equivalent to Mulliken's electronegativity, which is in turn proportional to Pauling's electronegativity

$$\frac{1}{2}(I+A) = \chi\,(\text{Mulliken}) \propto \chi\,(\text{Pauling}) \tag{3}$$

Assuming that the rest of the terms in Eq. (1) be independent of the halogen atoms, the linearity and parallelism obtained for the lowest lines suggest that coefficients c_x have a nearly constant value for all the alkyl halides in spite of different kinds of halogen and alkyl group.

However, we see from Fig. 5 that the plots of the second ionization energies show no parallelism, the line slope becomes rapidly gentle as the series ascends. In *n*-propyl and *n*-butyl halides, in particular it is interesting to note that the second lines are considerably flat.

Total Orbital Energies. Since the total sum of eigenvalues of a secular equation is mathematically equal to its diagonal sum, total orbital energies should be unchanged before and after taking orbital interaction into account. Assuming Koopmans' theorem, this

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9) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

TABLE 4. COMPARISON OF EXPERIMENTAL AND CALCULATED TOTAL ORBITAL ENERGIES (IN eV) FOR ALKYL HALIDES

		Exptl[a)]	Calcd[b)]	Difference
MeX	X=Cl	−68.83	−68.65	0.2
	Br	−65.89	−65.83	0.0
	I	−62.36	−62.57	−0.2
EtX	X=Cl	−95.19	−94.72	0.5
	Br	−92.42	−91.90	0.5
	I	−88.63	−88.64	0.0
n-PrX	X=Cl	−120.61	−120.79	−0.2
	Br	−117.64	−117.97	−0.4
	I	−114.40	−114.71	−0.3
n-BuX	X=Cl	−146.86	−146.86	0.0
	Br	−143.75	−144.03	−0.3
	I	−140.10	−140.77	−0.7

a) Obtained on the assumption of Koopmans' theorem using all the ionization energies observed for individual ethyl, *n*-propyl, and *n*-butyl halides (Tables 1—3). For the methyl halides, the ionization-energy values reported in Ref. 2 were used.

b) Calculated by substituting the orbital energies given in Table 5 into Eqs. (4)—(7).

sum rule may be applied to our ionization energy problem. For the individual alkyl halides we calculated total orbital energies using $-\{2(I_1)_{\mathrm{av}}+I_2+I_3+\cdots\}$ in the energy range studied. The resulting total energies thus obtained are shown in Table 4.

In interpreting these experimental total orbital energies, we considered that the orbitals under study are composed of several localized orbitals such as n(X), σ(C–X), σ(C–C), $\pi(\mathrm{CH_3})$, $\pi(\mathrm{CH_2})$, schematically shown in Fig. 7, and found that empirical values given in Table 5 are very suitable for these assumed orbitals. Total orbital energies were calculated with these values using the following equations

$$E(\mathrm{MeX}) = 2\varepsilon^0(n,\ \mathrm{X}) + \varepsilon^0(\sigma,\ \mathrm{C\text{-}X}) + 2\varepsilon^0(\pi,\ \mathrm{CH_3}) \tag{4}$$

$$E(\mathrm{EtX}) = E(\mathrm{MeX}) + \varepsilon^0(\sigma,\ \mathrm{C\text{-}C}) + \varepsilon^0(\pi,\ \mathrm{CH_2}) \tag{5}$$

$$E(n\text{-}\mathrm{PrX}) = E(\mathrm{MeX}) + 2\varepsilon^0(\sigma,\ \mathrm{C\text{-}C}) + 2\varepsilon^0(\pi,\ \mathrm{CH_2}) \tag{6}$$

$$E(n\text{-}\mathrm{BuX}) = E(\mathrm{MeX}) + 3\varepsilon^0(\sigma,\ \mathrm{C\text{-}C}) + 3\varepsilon^0(\pi,\ \mathrm{CH_2}) \tag{7}$$

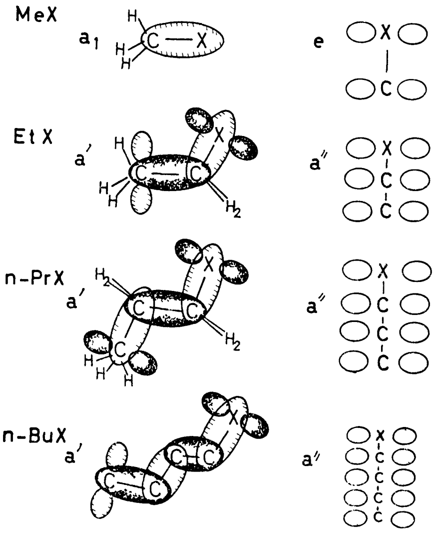

Fig. 7. Localized molecular orbitals used for the interpretation of the photoelectron data of the alkyl halides.

TABLE 5. ASSUMED ORBITAL ENERGIES (IN eV)

ε^0 (n, Cl) = −12.78[a)] ε^0 (σ, C–Cl) = −14.45[b)]
ε^0 (n, Br) = -11.83_5[a)] ε^0 (σ, C–Br) = −13.52[b)]
ε^0 (n, I) = -10.71_5[a)] ε^0 (σ, C–I) = −12.50[b)]
ε^0 (σ, C–C) = −11.75
ε^0 (π, $\mathrm{CH_3}$) = ε^0 (π, $\mathrm{CH_2}$) = −14.32

a) Taken from the $(I_1)_{\mathrm{av}}$ of the corresponding hydrogen halides reported in Ref. a) in Table 6.

b) Taken from the I_2 of the corresponding methyl halides reported in Ref. 2.

The calculated results are compared with the experimental ones in Table 4. It is interesting to see that the calculated total orbital energies are in good agreement with the experimental ones, strongly indicating that the molecular orbitals under consideration interact very slightly with inner orbitals such as C 2s and X *n*s orbitals.

The above agreements obtained for the total energy sums seem to support the existence of the concealed bands, whose ionization energy values are shown in parentheses in Tables 1—3.

As regards our estimation of the empirical energy values given in Table 5, the halogen non-bonding orbital energies were taken from the first mean ionization energies of molecules HX, shown in Table 6, since there is very little interaction between the non-bonding orbitals of these simplest halides and other valence orbitals. For C–X bands, their assumed unperturbed orbital energies were taken from orbital-energy values estimated from the second ionization energies of the methyl halides (Table 6), since the σ(C–X) orbitals belonging to a_1 symmetry do not interact with the n(X) and $\pi(\mathrm{CH_3})$ orbitals belonging to e symmetry and are considered to interact very slightly with inner orbitals of the same symmetry.

The $\pi(\mathrm{CH_3})$ orbital energy can not be determined directly from photoelectron spectra, since it always interacts with other orbitals to a considerable extent. However, from a comparison of the HX and MeX spectra, we can estimate the energy level of $\pi(\mathrm{CH_3})$

TABLE 6. PHOTOELECTRON DATA REPORTED FOR HYDROGEN AND METHYL HALIDES (IN eV)[a)]

	Lempka *et al.*[b)]			Ragel *et al.*[2)]		
	HCl	HBr	HI	MeCl	MeBr	MeI
$I_1(^2E_{3/2})$	12.74	11.67	10.38	11.29	10.53	9.50
$I_1(^2E_{1/2})$	12.82	12.00	11.05	11.37	10.85	10.13
$(I_1)_{\mathrm{av}}$	12.78	11.83_5	10.71_5	11.33	10.69	9.81_5
I_2				14.45	13.52	12.50
I_3 (J. T.)				15.47	15.14	14.79
I_3' (J. T.)				16.25	15.85	15.44
$(I_3)_{\mathrm{av}}$[c)]				15.86	15.49_5	15.11_5

a) Essentially the same results have been reported for the hydrogen halides by D. C. Frost, C. A. McDowell, and D. A. Vroom [*J. Chem. Phys.*, **46**, 4255 (1967)], and for the methyl halides by Potts *et al.* (Ref. 3) who did not describe values for I_3' (J. T.).

b) H. J. Lempka, T. R. Passmore, and W. C. Price, *Proc. Roy. Soc. Ser. A*, **304**, 53 (1968).

c) Taken as the center of gravity of the Jahn-Teller splittings.

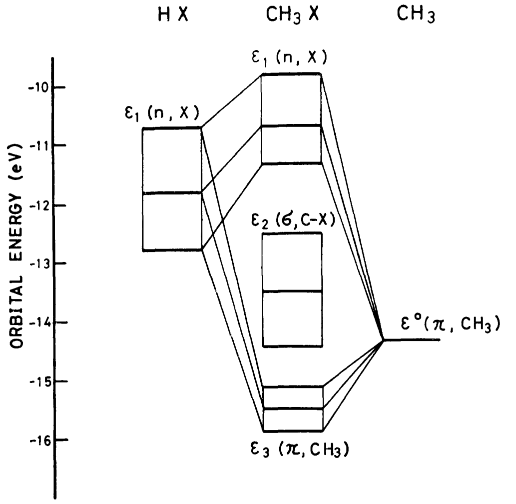

Fig. 8. Orbital energy levels of CH_3X (X=Cl, Br, and I), showing interactions of the n(X) and $\pi(CH_3)$ orbitals.

by considering that the first and third photoelectron bands result from an interaction of the halogen non-bonding and the CH_3 orbitals as shown in Fig. 8. Thus, assuming that

$$\{-I_1(CH_3X)\}_{av} + \{-I_3(CH_3X)\}_{av} = \{-I_1(HX)\}_{av} + \varepsilon^0(\pi, CH_3) \quad (8)$$

and using available data of ionization energy in the cases of X=Cl, Br, and I (see Table 6), we have $\varepsilon^0(\pi, CH_3) = -14.41$, -14.36 and -14.21 eV, respectively, with an average value of -14.32 eV.

The orbital energy of $\pi(CH_2)$ was assumed to be the same as that of $\pi(CH_3)$ for simplicity.

As shown in Fig. 9, the unperturbed C–C bonding

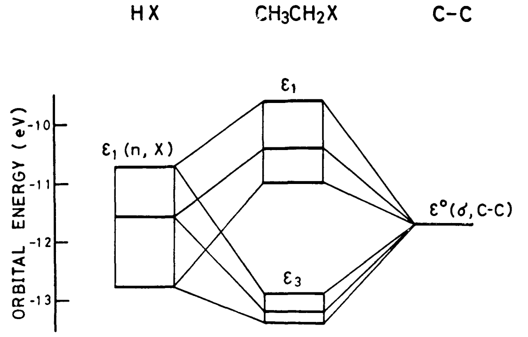

Fig. 9. Orbital energy levels ε_1 and ε_3 of C_2H_5X (X=Cl, Br, and I), showing interactions of the n(X) and σ(C–C) orbitals.

orbital energy $\varepsilon^0(\sigma, C\text{–}C)$ was estimated by taking the interaction between the C–C bonding and the halogen n'(X) orbitals of the ethyl halides into account. From the approximate equation

$$\{-I_1(EtX)\}_{av} + \{-I_3(EtX)\}_{av} = \{-I_1(HX)\}_{av} + \varepsilon^0(\sigma, C\text{–}C) \quad (9)$$

and with the available ionization energies, we obtained $\varepsilon^0(\sigma, C\text{–}C)$ values of -11.63, -11.80, and -11.82 eV in the cases of X=Cl, Br, and I, respectively, an average value of 11.75 eV being obtained.

From the agreements of the experimental and the calculated total orbital energies, we may conclude that our data of ionization energies shown in Tables 1—3 covers all the valence orbitals existing in the range higher than *ca.* -17 eV.

Assignments of Photoelectron Spectra. Orbital structures of the methyl halides are well understood and expressed approximately by[1-3)]

$$\cdots e(\pi, CH_3)^4 a_1(\sigma, C\text{–}X)^2 e(np\pi, X)^4$$

in decreasing order of ionization energy. We found that the lower-energy shifts of the first bands of methyl halides compared with those of hydrogen halides can well be interpreted in terms of the interactions between the n(X) orbital and the $\pi(CH_3)$ orbital which is assumed to possess an orbital energy of about -14.3 eV (Fig. 8). Calculated and experimental sums for the methyl halides are shown in Table 7, indicating a validity of the selection of the $\pi(CH_3)$ energy values.

Ethyl halides are of symmetry C_s, so that molecular orbitals are divided into two species a′ and a″. As shown in Figs. 9 and 10, interactions in species a′ are considered to occur mainly between n(X) and σ(C–C) and between σ(C–X) and $\pi(CH_3)$, while in species a″ the n'(X), $\pi'(CH_3)$ and $\pi'(CH_2)$ orbitals considerably mix with one another (see also Fig. 6).

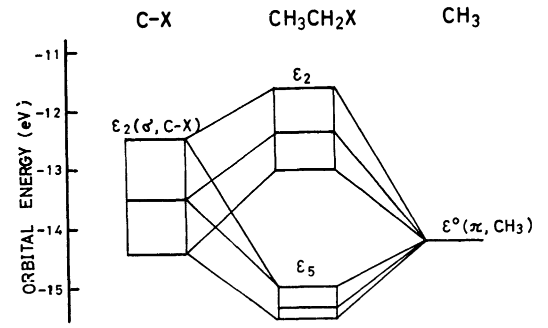

Fig. 10. Orbital energy levels ε_2 and ε_5 of C_2H_5X (X=Cl, Br, and I), showing interactions of the σ(C–X) and $\pi(CH_3)$ orbitals.

Using the sum rule mentioned before and the empirical energy values given in Table 5, it was found that the partial orbital-energy sums of {n(X) and σ(C–C)}, {σ(C–X) and $\pi(CH_3)$} and {n'(X), $\pi'(CH_3)$, and $\pi'(CH_2)$} are approximately equal to $-(I_1+I_3)$, $-(I_2+I_5)$ and $-(I'_1+I_4+I_6)$, respectively (Table 7). Good agreement of the partial sums of the calculated and experimental orbital energies makes it possible to assign the observed photoelectron bands of the ethyl halides. It might be concluded that I_2 and I_3 correspond to σ(C–X) and σ(C–C), respectively, with large contributions from $\pi(CH_3)$ and n(X), respectively. I_4, I_5, and I_6 can be assigned to $\pi'(CH_3)$, $\pi(CH_3)$ and $\pi'(CH_2)$, respectively. From the shapes of the first bands with spin-orbit splittings, it is not possible to distinguish the two bands corresponding to n(X) and n'(X) from each other which probably overlap closely.

For n-propyl halides, it is known that in gaseous phase there exist two types of rotational isomers, a *trans* form (symmetry C_s) and a *gauche* form (no symmetry).

Table 7. Assignments and partial orbital-energy sums (in eV)

Symmetry	Assignment		RCl	RBr	RI
	Methyl halides				
e	I_1, I_3	exptl[a]	−27.19	−26.18	−24.93
	n(X), π(CH$_3$)	calcd	−27.10	−26.15	−25.03
	Ethyl halides				
a'	I_1, I_3	exptl	−24.41	−23.64	−22.53
	n(X), σ(C-C)	calcd	−24.53	−23.58	−22.46
a'	I_2, I_5	exptl	−28.67	−27.84	−26.71
	σ(C-X), π(CH$_3$)	calcd	−28.77	−27.84	−26.82
a''	I_1', I_4, I_6	exptl	−42.11	−40.94	−39.38
	n'(X), π'(CH$_3$), π'(CH$_2$)	calcd	−41.42	−40.47	−39.35
	n-Propyl halides				
a'	I_2, I_5	exptl	−26.16	−25.61	−24.93
	σ(C$_2$-C$_3$), σ(C-X)	calcd	−26.20	−25.27	−24.25
a'	I_1, I_3, I_6	exptl	−38.16	−37.19	−36.00
	n(X), σ(C$_1$-C$_2$), π(CH$_3$)	calcd	−38.85	−37.90	−36.78
a''	I_1', I_4, I_7, I_8	exptl	−56.28	−54.84	−53.46
	n'(X), π'(CH$_3$), 2π'(CH$_2$)	calcd	−55.74	−54.79	−53.67
	n-Butyl halides				
a'	I_1, I_3, I_5	exptl	−36.11	−35.22	−33.91
	n(X), σ(C$_3$-C$_4$), σ(C$_1$-C$_2$)	calcd	−36.28	−35.33	−34.21
a'	I_2, I_6, I_8	exptl	−40.36	−39.53	−38.77
	σ(C$_2$-C$_3$), σ(C-X), π(CH$_3$)	calcd	−40.52	−39.59	−38.57
a''	I_1', I_4, I_7, I_9, I_{10}	exptl	−70.39	−68.99	−67.41
	n'(X), π'(CH$_3$), 3π'(CH$_2$)	calcd	−70.06	−69.11	−67.99

a) Used the values reported in Ref. 2.

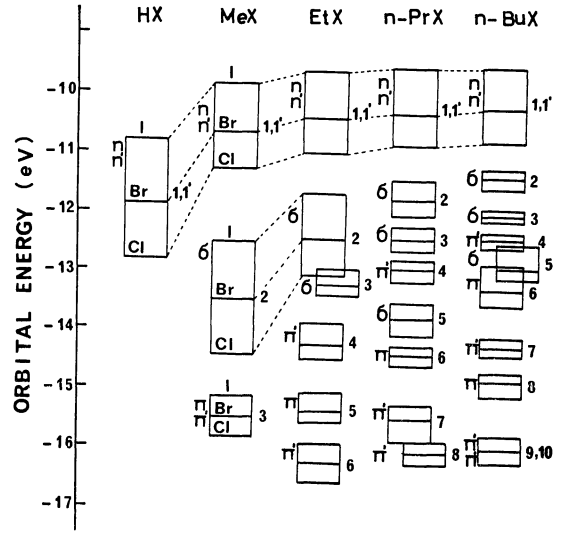

Fig. 11. Energy level diagram of the alkyl halides estimated from their photoelectron spectra, showing the effect of the successive methyl substitution.
In each block, the top line denotes RI, the middle line RBr and the bottom line RCl. Numbers 1,1′,2,3,········ correspond to the orbitals starting from the highest occupied orbital to the inner orbitals successively. Letters n, n', σ, π, and π' indicate the assignments for the orbitals (see Table 7 for more details).

In the *trans* configuration, molecular orbitals of these compounds are divided into species a′ and a″, and those belonging to species a′ are expected to separate roughly into two minor groups, as shown in Table 7, one composed of σ(C$_2$–C$_3$) and σ(C–X), and the other of n(X), σ(C$_1$–C$_2$), and π(CH$_3$). The *gauche* form was neglected in the present discussion for simplicity. The a″ species includes the n'(X), π'(CH$_3$), and two π'(CH$_2$) orbitals (Fig. 7). The present ionization-energy data of the series of n-propyl halides were well interpreted in terms of the orbital interactions summarized in Table 7, good agreement being obtained for the partial sums of the calculated and experimental orbital energies.

We obtained results for the n-butyl halides from a similar analysis (Table 7). Here, a *trans* configuration was again assumed for these compounds, so that molecular orbitals are divided into two species a′ and a″. The orbitals belonging to a′ can be expected to separate further into two minor groups with little interaction, one composed of n(X), σ(C$_3$–C$_4$), and σ(C$_1$–C$_2$), and the other of σ(C$_2$–C$_3$), σ(C–X), and π(CH$_3$). Other orbitals, n'(X), π'(CH$_3$) and three π'(CH$_2$) are easily seen to belong to a″. Calculated partial sums for these groups are in good agreement with the corresponding experimental sums as shown in Table 7. From the investigation mentioned above, the following assignments were concluded.

EtX a′: $(I_1, I_3) \rightarrow \{n(\mathrm{X}), \sigma(\mathrm{C\text{-}C})\}$
$(I_2, I_5) \rightarrow \{\sigma(\mathrm{C\text{-}X}), \pi(\mathrm{CH_3})\}$
a″: $(I_1', I_4, I_6) \rightarrow \{n'(\mathrm{X}), \pi'(\mathrm{CH_3}), \pi'(\mathrm{CH_2})\}$
n-PrX a′: $(I_2, I_5) \rightarrow \{\sigma(\mathrm{C_2\text{-}C_3}), \sigma(\mathrm{C\text{-}X})\}$
$(I_1, I_3, I_6) \rightarrow \{n(\mathrm{X}), \sigma(\mathrm{C_1\text{-}C_2}), \pi(\mathrm{CH_3})\}$
a″: $(I_1', I_4, I_7, I_8) \rightarrow \{n'(\mathrm{X}), \pi'(\mathrm{CH_3}), 2\pi'(\mathrm{CH_2})\}$

n-BuX a': $(I_1, I_3, I_5) \rightarrow \{n(\mathrm{X}), \sigma(\mathrm{C_3{-}C_4}), \sigma(\mathrm{C_1{-}C_2})\}$
$(I_2, I_6, I_8) \rightarrow \{\sigma(\mathrm{C_2{-}C_3}), \sigma(\mathrm{C{-}X}), \pi(\mathrm{CH_3})\}$
a'': $(I_1', I_4, I_7, I_9, I_{10}) \rightarrow \{n'(\mathrm{X}), \pi'(\mathrm{CH_3}), 3\pi'(\mathrm{CH_2})\}$

All the experimentally determined levels are shown in Fig. 11.

From the present study the second ionization in the n-propyl and n-butyl halides can be assigned to the $\sigma(\mathrm{C_2{-}C_3})$ orbital rather than the σ(C–X) orbital, although these orbitals are mixed considerably. It should be pointed out that this fact is reflected on the slope of the second lines shown in the correlation diagram in Fig. 5, whereas the slope of the corresponding lines of the methyl and ethyl halides are much steeper, indicating large contributions from the σ(C–X) orbitals.

We are thus able to infer the possible assignments of all the observed photoelectron bands to orbitals which can be interpreted in terms of the localized molecular orbitals schematically shown in Fig. 7. We may say in general that the total or partial sum of appropriate ionization energies gives an important clue to spectral assignment in photoelectron studies.