# Sum Rule Consideration of Molecular Photoelectron Spectra. Substituted Ethylenes

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The ionization-energy sum rule previously proposed has been applied to photoelectron spectra of three series of chloro-, bromo-, and methyl-substituted ethylenes $C_2H_{4-m}X_m$ ($m=1$ and 2; X=Cl, Br, and $CH_3$) in the He(I) region. The total sums of ionization energies were obtained in the p-type region and the partial sums of ionization energies were interpreted in terms of in-plane and out-of-plane molecular orbitals. The following conclusions have been deduced: (1) The experimental total and partial sums are almost constant in the *cis*-, *trans*-, and *iso*-disubstituted ethylenes. (2) The experimental total and partial sums linearly increase with increasing number of the substituents, the slopes leading to useful informations about orbital energies. (3) Such linear relationships are supported by CNDO/2 and MINDO/2 calculations. (4) The experimental total and partial sums are approximately reproduced in terms of several appropriate localized-molecular-orbital energies based on the photoelectron data of simplest molecules.

Molecular photoelectron spectroscopy provides a variety of vertical ionization energies associated with valence molecular orbitals.[1] Total and partial sums of vertical ionization energies in the He(I) region in various alkyl halides,[2-4] alcohols and amines[5] have previously been interpreted by Kimura *et al.* in terms of empirical energy values of appropriate p-type localized molecular orbitals (LO's) under Koopmans' theorem. A similar sum rule consideration has also been applied to ionization energies associated with out-of-plane orbitals in many planar skeletal unsaturated compounds,[6] and further extended to the He(II) region including all the valence molecular orbitals in mono-, di-, and tri-methylamine.[7] These sum rule considerations of ionization energies have been found to be very helpful for interpreting molecular photoelectron spectra.[2-8]

In the present paper we wish to report an application of the sum rule to chloro-, bromo-, and methyl-substituted ethylenes in the He(I) region, placing special emphasis on the total sum of ionization energies over all the p-type LO's and on the partial sums of ionization energies corresponding to the in-plane and out-of-plane LO's.

Photoelectron spectroscopy studies of substituted ethylenes have so far been carried out by many other workers.[1,9-16] The resulting photoelectron spectra, vertical ionization energies, and orbital assignments have been published in considerable detail. In the present sum rule consideration therefore we use the available complete sets of ionization energies.

## Sum Rule Consideration

In the present work we consider all the p-type LO's in the substituted ethylenes $C_2H_{4-m}X_m$ ($m=1$ and 2; X=Cl, Br, and $CH_3$). As previously done,[2-8] the p-type LO's used are: (1) nonbonding orbitals, $n_{Cl}$ and $n_{Br}$; (2) bonding orbitals, $\pi_{C=C}$, $\sigma_{C-Cl}$, $\sigma_{C-Br}$, $\sigma_{C-C}$, and $\sigma_{C=C}$; and (3) the pseudo $\pi$ orbitals of the methyl and methylene groups, $\pi_{CH_3}$ and $\pi_{CH_2}$. The numbers of p-type LO's in the substituted ethylenes studied are

Table 1. Numbers of *p*-type LO's in $C_2H_{4-m}X_m$

| Number of subst. ($m$) | In-plane (a′) | | | | Out-of-plane (a″) | | Total number of LO's |
|---|---|---|---|---|---|---|---|
| | $\sigma_{C=C}$ | $\pi_{CH_2}$ | $n_X$[a] | $\sigma_{C-X}$[a] | $\pi_{C=C}$ | $n_X$[a] | |
| 0 | 1 | 2 | | | 1 | | 4 |
| 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 |
| 2 {*cis*, *trans*} | 1 | | 2 | 2 | 1 | 2 | 8 |

a) When X is the methyl group, $n_X$ and $\sigma_{C-X}$ represent $\pi_{CH_3}$ and $\sigma_{C-C}$ respectively.

Table 2. Vertical ionization energies ($I_i$) in the p-type region

| | $I_1$ | $I_2$ | $I_3$ | $I_4$ | $I_5$ | $I_6$ | $I_7$ | $I_8$ |
|---|---|---|---|---|---|---|---|---|
| $C_2H_4$[a] | 10.51 | 12.85 | 14.66 | 15.87 | | | | |
| $C_2H_3Cl$[b] | 10.18 | 11.87 | 13.14 | (13.6) | 15.39 | 16.31 | | |
| *cis*-$C_2H_2Cl_2$[b] | 9.83 | 11.85 | 12.09 | 12.51 | 13.72 | (14.1) | 15.66 | 16.72 |
| *trans*-$C_2H_2Cl_2$[b] | 9.81 | 11.86 | 11.93 | 12.61 | 13.85 | 14.20 | 16.23 | 16.23 |
| *iso*-$C_2H_2Cl_2$[b] | 10.00 | 11.67 | 12.17 | 12.51 | (13.7) | 14.24 | 16.27 | 16.27 |
| $C_2H_3Br$[c] | 9.87 | 10.87 | 12.30 | 12.93 | 15.05 | 16.07 | | |
| *cis*-$C_2H_2Br_2$[c] | 9.63 | 10.74 | 11.23 | 11.53 | 12.86 | (13.2) | 14.83 | 16.35 |
| *trans*-$C_2H_2Br_2$[c] | 9.55 | 11.04 | 11.04 | 11.57 | 12.90 | (13.3) | 15.50 | 15.50 |
| *iso*-$C_2H_2Br_2$[c] | 9.78 | 10.73 | 11.23 | 11.60 | (13.0) | (13.0) | 15.20 | 15.90 |
| $C_2H_3(CH_3)$[d] | 10.03 | 12.31 | 13.23 | 14.48 | (14.8) | 15.90 | | |
| *cis*-$C_2H_2(CH_3)_2$[d] | 9.36 | 11.65 | 12.76 | (13.7) | 14.15 | (14.4) | (15.2) | 16.20 |
| *trans*-$C_2H_2(CH_3)_2$[d] | 9.37 | 11.96 | 12.79 | (13.2) | (14.5) | 15.17 | 15.17 | (15.6) |
| *iso*-$C_2H_2(CH_3)_2$[d] | 9.45 | 11.81 | 12.90 | (13.2) | (13.8) | 15.03 | (15.3) | (15.7) |

a) Ref. 11. b) Ref. 9. c) Ref. 14. d) Ref. 6.

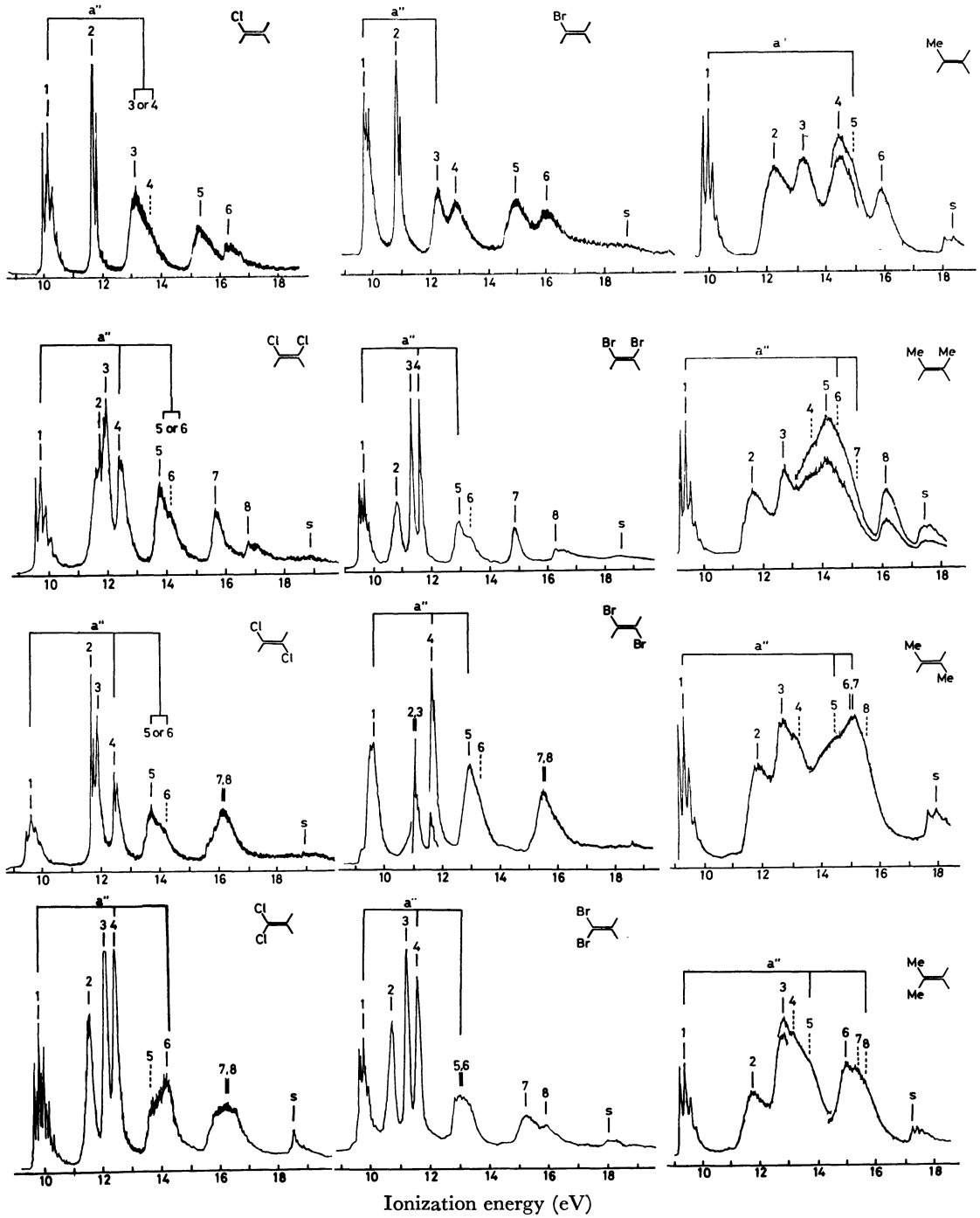


Fig. 1. Numbering of *p*-type ionization bands in He(I) photoelectron spectra of chloro-, bromo-, and methyl-substituted ethylenes.
The spectra of the chloro- and bromo-ethylenes are those reported by Wittel and Bock (Ref. 14) and the spectra of the methyl-substituted ethylenes are those reported previously by Kimura *et al.* (Ref. 6).
Out-of-plane bands are represented by a″ and s-type bands are by letters.

summarized in Table 1, indicating four, six, and eight p-type LO's in the un-, mono-, and di-substituted ethylenes, respectively. The present authors have previously indicated from several studies of alkyl compounds that all the photoelectron bands associated with p-type LO's lie below about 17—18 eV.[2-8] In order to show the numbering of the individual ionization bands, we illustrate the photoelectron spectra taken from the literatures in Fig. 1. The spectra of the series of chloro- and bromo-ethylenes in Fig. 1 are those from the paper of Wittel and Bock,[14] slightly modified in the numbering of the bands. The Wittel-Bock $I_7$ bands in *trans*- and *iso*-dichloroethylene and *trans*-dibromoethylene are designated as $I_7$ and $I_8$ in Fig. 1. The same numbers of ionization bands as those of p-type LO's can be recognized in the available photoelectron spectra in the region below about 17 eV in Fig. 1.

The vertical ionization energies used in the sum rule treatments are summarized in Table 2, in which the data for the chloro-, bromo-, and methyl-substituted ethylenes are those reported by Lake and Thompson,[9] by Wittel and Bock,[14] and by the present authors,[6] respectively. The values for $I_8$ in *trans*- and *iso*-dichloroethylene are set equal to those for $I_7$. The values in parentheses correspond to the shoulders which are indicated by vertical broken lines in Fig. 1.

*Experimental Total and Partial Sums.* The total sums of vertical ionization energies are taken over all the p-type region by

TABLE 3. EXPERIMENTAL TOTAL AND PARTIAL SUMS, COMPARED WITH CALCULATED ONES
(Values are shown in eV units and rounded to the next nearest 0.1 eV except for ethylene.)

| (LO's) → (Corresponding $I_i$'s) | Calcd. | Expt. |
|---|---|---|
| $CH_2$=$CH_2$ | $T$ = −53.89 | −53.89[a] |
| a′ ($2\pi_{CH_2}$, $\sigma_{C=C}$)→($I_2$,$I_3$,$I_4$) | $P'$ = −43.38 | −43.38[a] |
| a″($\pi_{CC}$)→($I_1$) | $P''$= −10.51 | −10.51[a] |
| CHCl=$CH_2$ | $T$ = −80.3 | −80.5 |
| a′ ($n_{Cl}$, $\pi_{CH_2}$, $\sigma_{CCl}$, $\sigma_{C=C}$)→($I_2$,$I_3$,$I_5$,$I_6$)[b] | $P'$ = −56.8 | −56.7 |
| →($I_2$,$I_4$,$I_5$,$I_6$)[c,d] | | −57.2 |
| a″($\pi_{CC}$, $n_{Cl}$)→($I_1$,$I_4$)[b] | $P''$= −23.6 | −23.8 |
| →($I_1$,$I_3$)[c,d] | | −23.3 |
| *cis*-CHCl=CHCl | $T$ = −106.8 | −106.5 |
| a′ ($2n_{Cl}$, $2\sigma_{CCl}$, $\sigma_{C=C}$)→($I_2$,$I_3$,$I_5$,$I_7$,$I_8$)[b,d] | $P'$ = −70.2 | −70.0 |
| →($I_2$,$I_3$,$I_6$,$I_7$,$I_8$)[c] | | −70.4 |
| a″($\pi_{CC}$, $2n_{Cl}$)→($I_1$,$I_4$,$I_6$)[b,d] | $P''$= −36.6 | −36.4 |
| →($I_1$,$I_4$,$I_5$)[c] | | −36.1 |
| *trans*-CHCl=CHCl | $T$ = −106.8 | −106.7 |
| a′ ($2n_{Cl}$, $2\sigma_{CCl}$, $\sigma_{C=C}$)→($I_2$,$I_3$,$I_5$,$I_7$,$I_8$)[b,d] | $P'$ = −70.2 | −70.1 |
| →($I_2$,$I_3$,$I_6$,$I_7$,$I_8$)[c] | | −70.5 |
| a″($\pi_{CC}$, $2n_{Cl}$)→($I_1$,$I_4$,$I_6$)[b,d] | $P''$= −36.6 | −36.6 |
| →($I_1$,$I_4$,$I_5$)[c] | | −36.3 |
| $CCl_2$=$CH_2$ | $T$ = −106.4 | −106.8 |
| a′ ($2n_{Cl}$, $\pi_{CH_2}$, $\sigma_{CCl}$, $\sigma_{C=C}$)→($I_2$,$I_3$,$I_5$,$I_7$,$I_8$)[b,c,d] | $P'$ = −69.8 | −70.1 |
| a″($\pi_{CC}$, $2n_{Cl}$)→($I_1$,$I_4$,$I_6$)[b,c,d] | $P''$= −36.6 | −36.8 |
| CHBr=$CH_2$ | $T$ = −77.1 | −77.1 |
| a′ ($n_{Br}$, $\sigma_{CBr}$, $\pi_{CH_2}$, $\sigma_{C=C}$)→($I_2$,$I_4$,$I_5$,$I_6$)[c,e] | $P'$ = −54.7 | −54.9 |
| a″($\pi_{CC}$, $n_{Br}$)→($I_1$,$I_3$)[c,e] | $P''$= −22.4 | −22.2 |
| *cis*-CHBr=CHBr | $T$ = −100.4 | −100.4 |
| a′ ($2n_{Br}$, $2\sigma_{CBr}$, $\sigma_{C=C}$)→($I_2$,$I_3$,$I_6$,$I_7$,$I_8$)[c] | $P'$ = −66.1 | −66.4 |
| →($I_2$,$I_4$,$I_5$,$I_7$,$I_8$)[e] | | −66.3 |
| a″($\pi_{CC}$, $2n_{Br}$)→($I_1$,$I_4$,$I_5$)[c] | $P''$= −34.3 | −34.0 |
| →($I_1$,$I_3$,$I_6$)[e] | | −34.1 |
| *trans*-CHBr=CHBr | $T$ = −100.4 | −100.4 |
| a′ ($2n_{Br}$, $2\sigma_{CBr}$, $\sigma_{C=C}$)→($I_2$,$I_3$,$I_6$,$I_7$,$I_8$)[c] | $P'$ = −66.1 | −66.4 |
| →($I_2$,$I_4$,$I_5$,$I_7$,$I_8$)[e] | | −66.5 |
| a″($\pi_{CC}$, $2n_{Br}$)→($I_1$,$I_4$,$I_5$)[c] | $P''$= −34.3 | −34.0 |
| →($I_1$,$I_3$,$I_6$)[e] | | −33.9 |
| $CBr_2$=$CH_2$ | $T$ = −100.1 | −100.4 |
| a′ ($2n_{Br}$, $\pi_{CH_2}$, $2\sigma_{CBr}$)→($I_2$,$I_3$,$I_6$,$I_7$,$I_8$)[c] | $P'$ = −65.8 | −66.1 |
| a″($\pi_{CC}$, $2n_{Br}$)→($I_1$,$I_4$,$I_5$)[c] | $P''$= −34.3 | −34.4 |
| CH($CH_3$)=$CH_2$ | $T$ = −80.7 | −80.8 |
| a′ ($\sigma_{C-C}$, $\pi_{CH_3}$, $\pi_{CH_2}$, $\sigma_{C=C}$)→($I_2$,$I_3$,$I_4$,$I_6$)[f,g,h] | $P'$ = −55.9 | −55.9 |
| a″($\pi_{CC}$, $\pi_{CH_3}$)→($I_1$,$I_5$)[f,g,h] | $P''$= −24.8 | −24.8 |
| *cis*-CH($CH_3$)=CH($CH_3$) | $T$ = −107.5 | −107.4 |
| a′ ($2\sigma_{C-C}$, $2\pi_{CH_3}$ $\sigma_{C=C}$)→($I_2$,$I_3$,$I_4$,$I_5$,$I_8$)[f,g,h] | $P'$ = −68.4 | −68.5 |
| a″($\pi_{CC}$, $2\pi_{CH_3}$)→($I_1$,$I_6$,$I_7$)[f,g,h] | $P''$= −39.1 | −39.0 |
| *trans*-CH($CH_3$)=CH($CH_3$) | $T$ = −107.5 | −107.8 |
| a′ ($2\sigma_{C-C}$, $2\pi_{CH_3}$, $\sigma_{C=C}$)→($I_2$,$I_3$,$I_4$,$I_{7(6)}$,$I_8$)[g,h] | $P'$ = −68.4 | −68.7 |
| a″($\pi_{CC}$, $2\pi_{CH_3}$)→($I_1$,$I_5$,$I_{6(7)}$)[g,h] | $P''$= −39.1 | −39.0 |
| C($CH_3$)$_2$=$CH_2$ | $T$ = −107.2 | −107.2 |
| a′ ($2\sigma_{C-C}$, $2\pi_{CH_3}$, $\pi_{CH_2}$)→($I_2$,$I_3$,$I_4$,$I_6$,$I_7$)[f,g,h] | $P'$ = −68.1 | −68.2 |
| a″($\pi_{CC}$, $2\pi_{CH_3}$)→($I_1$,$I_5$,$I_8$)[f,g,h] | $P''$= −39.1 | −39.0 |

a) Data in Ref. 11 were used. b) Klasson and Manne (Ref. 18). c) Wittel and Bock (Ref. 14). d) Kato *et al.* (Ref. 17). e) Chadwick *et al.* (Ref. 12). f) The present MINDO/2 calculations. g) Katrib and Rabalais (Ref. 13). h) White *et al.* (Ref. 16).

Table 4. Average $\alpha$ values (in eV) obtained with the experimental total and partial sums

| Series | | $\alpha$ | $\alpha'$ | $\alpha''$ |
|---|---|---|---|---|
| $C_2H_{4-m}Cl_m$ | ($m$=0—2) | −26.44±0.07 | −13.34±0.01 | −13.11±0.06 |
| $C_2H_{4-m}Br_m$ | ($m$=0—2) | −23.24±0.01 | −11.48±0.04 | −11.78±0.06 |
| $C_2H_{4-m}(CH_3)_m$ | ($m$=0—2) | −26.82±0.06 | −12.54±0.05 | −14.26±0.01 |

$$T_{\text{expt}} = -\sum_{i}^{\text{all}} I_i \quad (1)$$

and the experimental partial sums associated with the in-plane and out-of-plane LO's, $P'$ and $P''$, respectively, are obtained by

$$P'_{\text{expt}} = -\sum_{i}^{a'} I_i \quad \text{and} \quad P''_{\text{expt}} = -\sum_{i}^{a''} I_i \quad (2)$$

which are based on the available symmetry assignments. The results of the experimetal total and partial sums obtained by Eqs. (1) and (2) are summarized in Table 3. Since different kinds of orbital assignments have been proposed for the chloro- and bromo-ethylenes,[12,14,17,18] we took two kinds of possible combinations of $I_i$ into account in the partial sums as shown in Table 3.

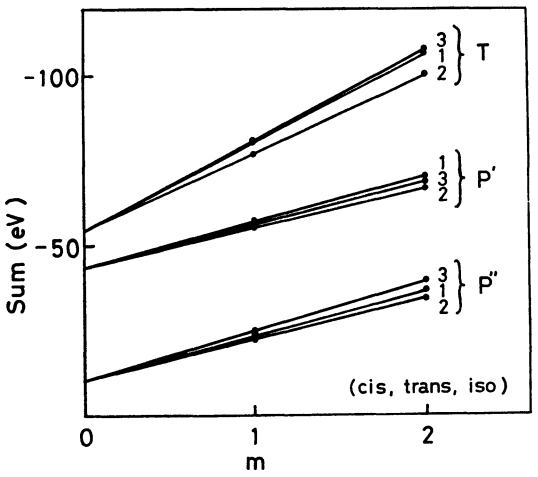


Fig. 2. Plot of the experimental total and partial sums of vertical ionization energies against the number of substituents in series of (1) chloro-, (2) bromo-, and (3) methyl-substituted ethylenes.

In Fig. 2 the experimental values for $T$, $P'$, and $P''$ are plotted against the number ($m$) of substituents, indicating excellent linear relationships. The straight lines (solid lines) in Fig. 2 are drawn so as to fit the experimental data. The slope of the straight lines represents the variation of the total and partial sums with increasing number of substituents.

*Calculated Total and Partial Sums.* As shown previously,[2-8] the total and partial sums in the substituted ethylenes may be expressed in terms of empirical LO energies as follows,

$$T_{\text{calc}} = P'_{\text{calc}} + P''_{\text{calc}} \quad (3)$$

$$P'_{\text{calc}} = m\varepsilon_{n(X)} + m\varepsilon_{\sigma(C-X)} + (2-m)\varepsilon_{\pi(CH_2)} + \varepsilon_{\sigma(C=C)} \quad (4)$$

$$P''_{\text{calc}} = m\varepsilon_{n(X)} + \varepsilon_{\pi(C=C)} \quad (5)$$

When X is the methyl group, n(X) and $\sigma$(C-X) in Eqs. (4) and (5) represent $\pi(CH_3)$ and $\sigma$(C–C), respectively. From Eqs. (4) and (5), therefore the successive differences $\alpha'$ and $\alpha''$ in the partial sums may be expressed as follows

$$\alpha' = \varepsilon_{n(X)} + \varepsilon_{\sigma(C-X)} - \varepsilon_{\pi(CH_2)} \quad (6)$$

$$\alpha'' = \varepsilon_{n(X)} \quad (7)$$

On the other hand, the successive differences in $T$, $P'$, and $P''$ may be experimentally obtained from the slopes of the straight lines shown in Fig. 2. The resulting average values for $\alpha$, $\alpha'$, and $\alpha''$ are summarized in Table 4, the upper combination of $I_i$ being used in the case in which two possible combinations of $I_i$ are shown in Table 3.

Table 5. Empirical energies of p-type LO's (in eV)

| | | | |
|---|---|---|---|
| a′ (in-plane) | | | |
| $n_{Cl}$= | $n_{Br}$= | $\pi_{CH_3}$= | $\pi_{CH_2}$= |
| −13.05 | −11.89 | −14.30 | −14.36 |
| $\sigma_{C-Cl}$= | $\sigma_{C-Br}$= | $\sigma_{C-C}$= | $\sigma_{C=C}$= |
| −14.70 | −13.82 | −12.58 | −14.66 |
| a″ (out-of-plane) | | | |
| $n_{Cl}$= | $n_{Br}$= | $\pi_{CH_3}$= | $\pi_{C=C}$= |
| −13.05 | −11.89 | −14.30 | −10.51 |

The values for $\varepsilon$'s used in the sum rule treatments are summarized in Table 5, which were selected on the basis of the vertical ionization energies of simple molecules as follows. The energies of n(Cl) and n(Br) were taken from the mean values of the first and second ionization energies of molecular chlorine and bromine, respectively.[19] The energies of $\pi$(C=C) and $\sigma$(C=C) were taken from the first and third ionization energies of ethylene, respectively.[11] The energy of $\pi(CH_2)$ was taken from the mean value of the second and fourth ionization energies of ethylene.[11] The energy of $\pi(CH_3)$ was determined from the ionization energies of methyl halides as described previously.[2] The energies of $\sigma$(C–Cl), $\sigma$(C–Br), and $\sigma$(C–C) were deduced by Eq. (6) from the experimental $\alpha'$ values shown in Table 4.

With all these energy parameters the total sums ($T$) and the in-plane and out-of-plane partial sums ($P'$ and $P''$) were calculated by Eqs. (3)—(5), the results being compared with the experimental results in Table 3.

## Discussion

The following three points may be pointed out on the experimental total and partial sums. (1) Good linear relationships can be seen between the sums ($T$, $P'$, and $P''$) and the number of substituents. (2) The total and partial sums of the *cis*-, *trans*-, and *iso*-isomers in each series are very close to one another. (3) The effects of the chloro-, bromo-, and methyl-substitutions on the total and partial sums are very similar, as seen from Fig. 2.

Previously,[8] a good linearity was indicated between such total sums and the number of chlorine atoms in a

series of chloroethanes $C_2H_{6-m}Cl_m$ ($m$=0—6), and a value of −14.90 eV was deduced for σ(C–Cl), differing slightly from the value of −14.70 eV found here in the chloroethylenes. In the present work, the linearities have been found not only for the total sums but also for the partial sums.

From Eq. (7) it is seen that the successive difference $\alpha''$ is equivalent to $\varepsilon_{n(X)}$, so that the $\alpha''$ values of −13.11, −11.78 and −14.26 eV in Table 4 may be regarded as the orbital energies for n(Cl), n(Br), and $\pi(CH_3)$, respectively. It is interesting to note that these values are very close to those given in Table 5 which were determined from the photoelectron data of the simple molecules.

In the previous study of alkyl alcohols and amines (ROH and $RNH_2$; R=methyl to *n*-butyl),[5] we obtained an average difference of −26.04 eV in the total sums for the successive substitution of the $CH_3$ group. A similar value $\alpha_{av.}$=−26.07 eV was obtained in a series of alkyl halides (RX: R=methyl to *n*-butyl; X=Cl, Br, and I).[2] Furthermore, using available ionization energies of several alkanes (methane, ethane, propane, isobutane, and neopentane),[20] we may obtain a value of $\alpha_{av.}$=−26.0 eV. In these saturated alkyl compounds, therefore, the differences in $T$ by the successive $CH_3$ substitutions are found to be −26.0——26.1 eV, close to the sum of −11.75 eV and −14.30 eV which have previously been proposed for $\sigma_{C-C}$ (in alkyl compounds) and $\pi_{CH_2}$, respectively.[2-5] For the methyl-substituted ethylenes studied here, however, we obtained a value of $\alpha_{av.}$=−26.82 eV which leads to a value of −12.58 eV for $\sigma_{C-C}$ involving the $sp^2$ carbon as given in Table 5.

The α value of −26.44 eV in the series of chloroethylenes is fairly close to that (−26.69 eV) previously obtained in a series of chloroethanes.[8] The energies of −14.70 and −13.82 eV deduced for $\sigma_{C-Cl}$ and $\sigma_{C-Br}$, respectively, in the present work are fairly close to those (−14.45 and −13.52 eV, respectively) previously estimated from the second ionization energies of methyl chloride and bromide, respectively.[2] As seen from Eq. (7), the $\alpha''$ values of −13.11, −11.78, and −14.26 eV in Table 4 are equivalent to $\varepsilon_{n(Cl)}$, $\varepsilon_{n(Br)}$, and $\varepsilon_{\pi(CH_3)}$, respectively, in excellent agreement with those (−13.05, −11.89, and −14.30 eV, respectively) determined from the simple molecules.

From the present study it has been found that the experimental total and partial sums of the *iso*-isomers are almost the same as those of the *cis*- and *trans*-isomers. Equation (4) however does not hold for the *iso*-compounds. One of three LO's associated with the carbon $sp^2$ orbitals in the $CCl_2$ group in 1,1-dichloroethylene should be of s-type. In calculating $P'$, therefore, one of the three in-plane p-type LO's (two σ(C–Cl) and one σ(C=C)) should be removed as an s-type LO. It is not unambiguous however to decide which one is of s-type. As shown in the combinations of LO's in Table 3, we removed one σ(C–Cl) in 1,1-dichloroethylene and σ(C=C) in 1,1-dibromoethylene and isobutene. The numbers of in-plane p-type LO's in the *iso*-isomers are of course the same as those in the *cis*- and *trans*-isomers.

Only the ionization energy data shown in Table 2 were used in the present sum rule considerations. Other complete sets of ionization energies reported for the chloroethylenes by Jonathan *et al.*[10] and Wittel and Bock[14] and for the bromoethylenes by Chadwick *et al.*[12] were also employed, and it was found that essentially the same results as above on the total and partial sums may be obtained.

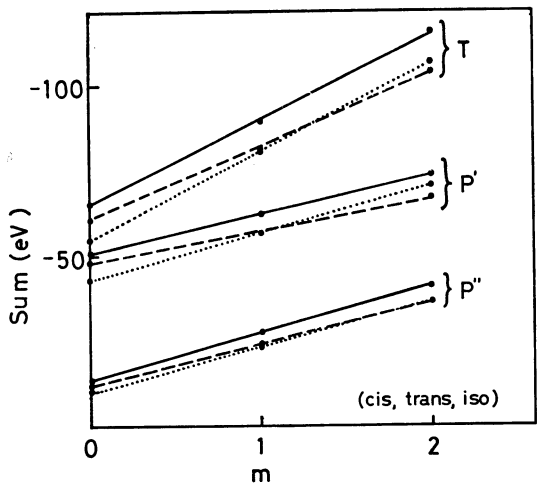


Fig. 3. Plot of theoretical total and partial sums obtained by CNDO/2 method against the number of chlorine atoms in a series of chloroethylenes.
The results multiplied by 0.85 (solid lines) and the results of the 4-eV correction (broken lines) are compared with the experimental ones (dotted lines).

In the present work we also investigated the relationship between the total (and partial) sums and the number of substituents using CNDO/2 method[21] and MINDO/2 method[22] under the Koopmans' theorem. The CNDO/2 results of $T$, $P'$, and $P''$ for the series of chloroethylenes are plotted against the number of chlorine atoms in Fig. 3, the solid lines indicating the results multiplied by 0.85. The broken lines in Fig. 3 show the results reduced by 4 eV in each orbital. It is interesting to note in Fig. 3 that good linear relationships between the sum and the number of chlorine

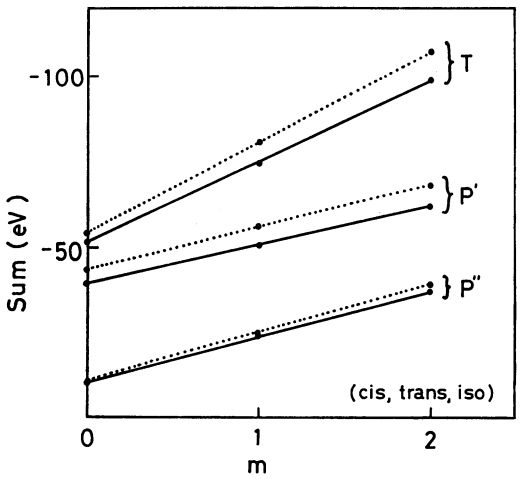


Fig. 4. Plot of theoretical total and partial sums obtained by MINDO/2 method against the number of $CH_3$ groups in a series of methyl-substituted ethylenes.
Dotted lines represent the experimental results.

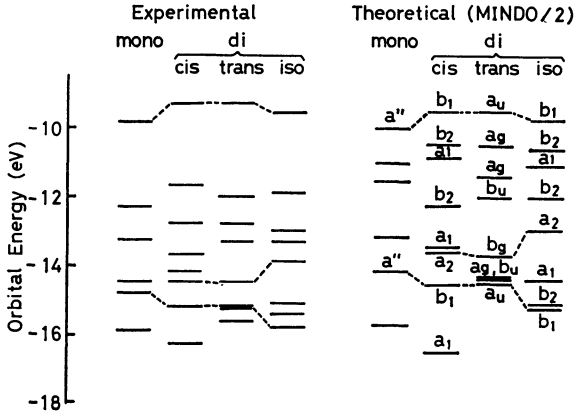


Fig. 5. Experimental and theoretical orbital level diagrams of the methyl-substituted ethylenes.

atoms can be seen and that the calculated results multiplied by 0.85 are approximately parallel to the experimental lines (dotted lines). The MINDO/2 results of $T$, $P'$, and $P''$ for the methyl-substituted ethylenes are shown in Fig. 4, again indicating good linearities and parallelisms between calculation and experiment. The linearities between the partial sums and the number of substituents have been found for the first time in the present work.

Theoretical orbital energy diagrams obtained by the MINDO/2 method for the methyl-substituted ethylenes are shown in Fig. 5, compared with those of the experimental diagrams. The out-of-plane levels in Fig. 5 are connected by broken lines. As can be seen from Fig. 5, it may be pointed out that the variation of the out-of-plane levels in going from ethylene to *iso*-butylene is well reproduced by the MINDO/2 calculations.

Finally, the following point should be mentioned in connection with Koopmans' theorem. Koopmans' theorem has been assumed in the present orbital energy considerations using the experimental ionization energies. However, if we consider each empirical value in Table 5 (without the negative sign) as a hypothetical ionization energy of an electron from the original unperturbed p-type LO, the present sum rule consideration may be thought as an "additivity rule of ionization energy." In such a standpoint, Koopmans' theorem is unnecessary. Potts *et al.*[23] have indicated that the total sums of ionization energies associated with s- and p-type photoelectron bands in many aliphatic compounds may be reproduced in terms of atomic energy parameters on the basis of an idea of additivity rule. Most striking difference between the present sum rule consideration and the additivity rule consideration of Potts *et al.*[23] is that the former depends on the LO's whose energies are based on the molecular photoelectron spectra of simplest molecules, whereas the latter depends on the atomic parameters.

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