MO Interpretation of Some Physico-chemical Properties of Alkyl Compound

By Teijiro YONEZAWA, Hiroshi KATO, Hazime SAITO
and Kenichi FUKUI

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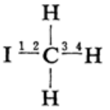
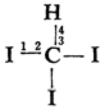
A few quantum-mechanical investigations of the electronic structure of halomethane molecules have been made by the VB method, discussing the ionic character of carbon-halogen bonds in these compounds[1], and also by a simple two-center LCAO MO treatment[2].

In a previous paper[3], we discussed the electronic structures and reactivities of some halomethane molecules using the simple LCAO MO treatment for saturated compounds we had previously reported. In this treatment, the molecular orbitals of halomethanes are given by the linear combinations of the atomic (or of hybridized) orbitals of the composite atoms in a molecule. It has been made clear by the microwave spectral data that the bond lengths, especially that of the C–X bond, and also the valence angles vary remarkably among CH_3X, CH_2X_2, CHX_3 and CX_4. Also, the double bond character, which has been particularly recognized in CX_4 molecules, has been disregarded, since the main purpose of our paper is to a verification of the validity of our simple LCAO MO treatment. For the sake of simplicity, overlap integrals are neglected and the same values as in the previous paper[3] are adopted in the present paper for Coulomb and resonance integrals. These values

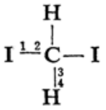
TABLE I. THE CALCULATED ORBITAL ENERGIES AND ELECTRON DISTRIBUTIONS IN IODOMETHANES



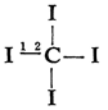
Orbital energy	Electron distribution			
	$(C_1^j)^2$	$(C_2^j)^2$	$(C_3^j)^2$	$(C_4^j)^2$
$\alpha-1.37223\beta$*	0	0	0.3545	0.3122
$\alpha-1.08150\beta$	0.0183	0.1430	0.1093	0.1702
$\alpha-0.33688\beta$	0.2739	0.5249	0.0010	0.0646
$\alpha+0.69454\beta$	0.6854	0.2117	0.0137	0.0207
$\alpha+0.83223\beta$*	0	0	0.3122	0.3545
$\alpha+1.60384\beta$	0.0255	0.1160	0.2093	0.0778



Orbital energy	Electron distribution			
	$(C_1^j)^2$	$(C_2^j)^2$	$(C_3^j)^2$	$(C_4^j)^2$
$\alpha-1.29580\beta$	0.4745	0.4708	0.0166	0.0016
$\alpha-0.61637\beta$*	0	0	0.5241	0.1455
$\alpha-0.02709\beta$	0.1004	0.0025	0.1177	0.1813
$\alpha+0.67638\beta$*	0	0	0.1455	0.5241
$\alpha+0.76110\beta$	0.2870	0.2191	0.0522	0.1124
$\alpha+1.44152\beta$	0.1378	0.3074	0.1469	0.0380



Orbital energy	Electron distribution			
	$(C_1^j)^2$	$(C_2^j)^2$	$(C_3^j)^2$	$(C_4^j)^2$
$\alpha-1.37223\beta$	0	0	0.2659	0.2341
$\alpha-1.20359\beta$	0.0055	0.0499	0.2020	0.2427
$\alpha-0.61637\beta$	0.1096	0.3931	0	0
$\alpha-0.16738\beta$	0.1944	0.2227	0.0001	0.0828
$\alpha+0.67638\beta$	0.3931	0.1069	0	0
$\alpha+0.72067\beta$	0.2721	0.0996	0.0528	0.0754
$\alpha+0.83223\beta$	0	0	0.2341	0.2659
$\alpha+1.53029\beta$	0.0281	0.1278	0.2451	0.0991



Orbital energy	Electron distribution	
	$(C_1^j)^2$	$(C_2^j)^2$
$\alpha-0.61637\beta$**	0.1603	0.5897
$\alpha+0.09500\beta$	0.1881	0.0619
$\alpha+0.67637\beta$**	0.5897	0.1603
$\alpha+1.32401\beta$	0.0619	0.1881

* Doubly degenerate
** Three fold degenerate

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[1] E. Hamano, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 985 (1956); **79**, 362 (1958).

[2] G. Del Re, *J. Chem. Soc.*, **1958**, 4031.

[3] K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **34**, 442, 1111 (1961).

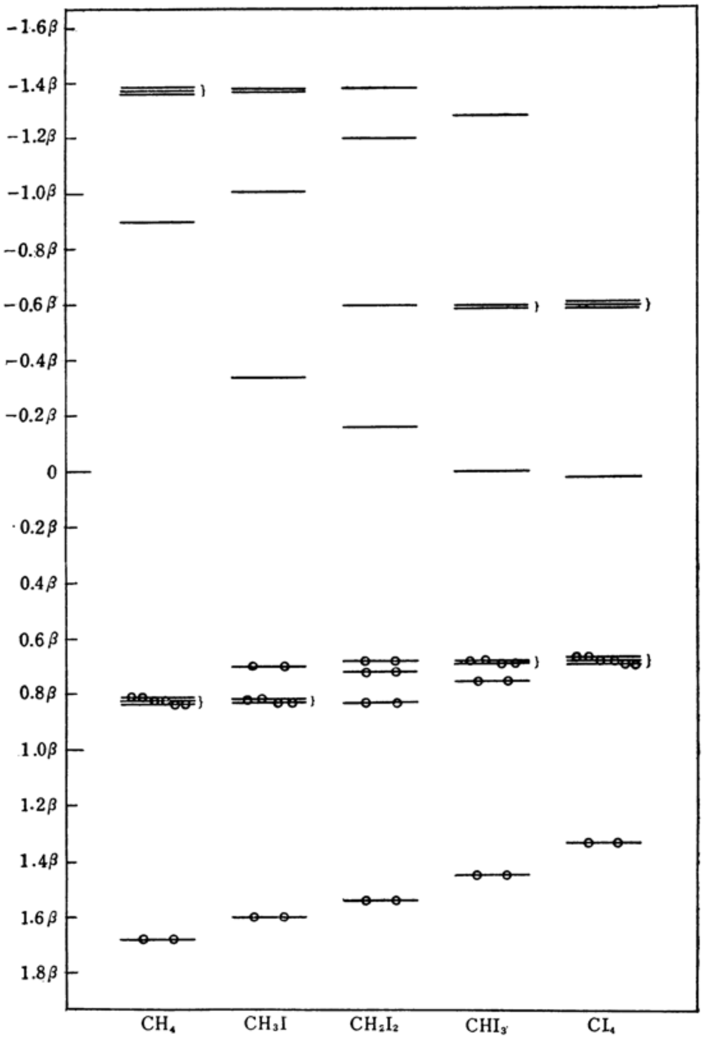

Fig. 1. The orbital energies of iodomethanes.

are summarized as follows:

$\alpha_C = \alpha$

$\alpha_H = \alpha - 0.2\beta$

$\alpha_F = \alpha + 0.9\beta$

$\alpha_{Cl} = \alpha + 0.5\beta$

$\alpha_{Br} = \alpha + 0.45\beta$

$\alpha_I = \alpha + 0.4\beta$

$\beta_{CC} = \beta$

$\beta_{\text{-C-}} = 0.34\beta$

$\beta_{CH} = 1.1\beta$

$\beta_{CF} = 0.5\beta$

$\beta_{CCl} = 0.65\beta$

$\beta_{CBr} = 0.58\beta$

$\beta_{CI} = 0.53\beta$

Since the lone pair electrons at halogen atoms are not explicitly taken into account in the present treatment, the energy of this non-bonding orbital is estimated from the experimental values of the ionization potentials assigned by McDowell⁴⁾. The estimated energies of non-bonding orbitals at fluorine, chlorine, bromine and iodine atoms are represented in terms of α and β, which are the standard Coulomb and resonance integrals respectively in σ-electronic systems*.

Electronic Structure of Halomethanes

The calculated energy levels and electronic distributions for iodine derivatives of methane are listed in Table I, while a diagram indicating the change in the energy levels is given in Fig. 1. As was mentioned in our previous paper³⁾, the bonding electrons tend to be

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4) D. C. Frost and C. A. McDowell, *Proc. Roy. Soc.*, **A241**, 194 (1957).

* The estimated values of the lone pair orbital energy of halogen atoms (ε_X) are:

$\varepsilon_F = \alpha + 1.1\beta$

$\varepsilon_{Cl} = \alpha + 0.5\beta$

$\varepsilon_{Br} = \alpha + 0.4\beta$

$\varepsilon_I = \alpha + 0.2\beta$

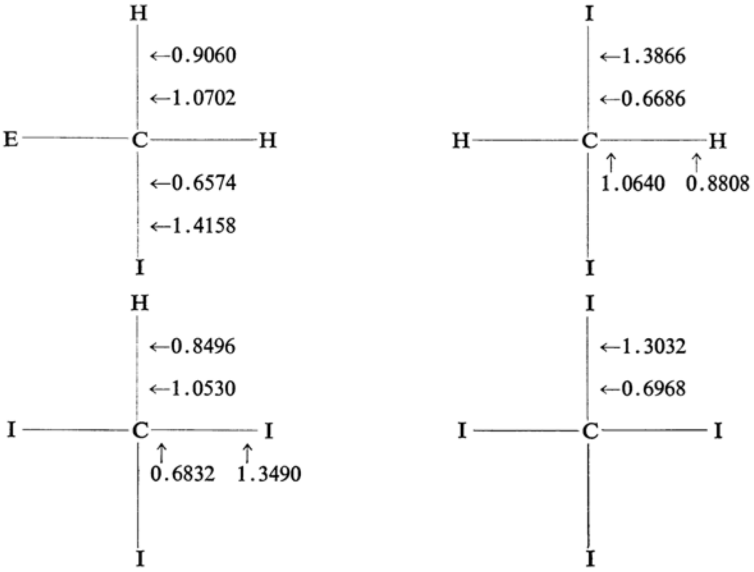

Fig. 2. The σ electronic densities of iodomethanes.

localized in the particular bonds in each molecular orbital; the bonding electrons in the highest occupied and the lowest vacant orbital are localized mainly in the C–I bond, and those in the next highest occupied orbital, in the C–H bond.

As to the orbital energies, it is seen that the larger the number of substituted halogen atoms, the lower the lowest vacant orbital energy, as is shown in Fig. 1.

In Fig. 2, the calculated total σ-electron densities in iodomethanes are presented.

As a general tendency, the ionic character interpreted from the present molecular orbital treatment decreases in the order: $CH_3X > CH_2X_2 > CHX_3 > CX_4$. This order agree with that indicated by the experimental results of pure quadrupole coupling constants.

Based upon these findings, a molecular orbital interpretation of such physico-chemical properties of halomethane molecules as n-σ^* absorption, PQR coupling constants, and proton chemical shifts are presented.

n-σ^* Absorption.—The theoretical interpretation of the n-σ^* absorption of halomethane molecules, especially of iodine and chlorine compounds, has been argued by Mulliken[5], Walsh[6], and Nagakura et al.[7] The longest-wavelength absorption in halomethanes is due to the excitation of an electron from the lone pair electron orbital to the lowest vacant orbital. The calculated energy differences between the lone pair electron orbital and the vacant orbital in these compounds are listed in Table II, together with the observed wavelengths[8]. In the series of halomethanes substituted for by a certain number of halogen atoms of the same kind, a parallelism is found between experimental and calculated values; the calculated values show a tendency for the wavelength of the absorption spectrum to increase with the number of halogen atoms in halomethanes, all in accordance with experimental findings. When a comparison is made among the molecules with different halogen atoms, however, a discrepancy between the observed and the calculated results is found. This discrepancy may

TABLE II. THE CALCULATED VALUES OF ENERGY DIFFERENCE BETWEEN TRANSITION AND OBSERVED WAVELENGTHS

Compound	Calcd. (in unit of $-\beta$)	Obs. (Å)[8]
CH_3Cl	0.8998	1610∼1540
CH_2Cl_2	0.7287	—
$CHCl_3$	0.5810	1830<2200
CCl_4	0.4401	—
CH_3Br	0.7611	2040
CH_2Br_2	0.5897	2190 (2208)
$CHBr_3$	0.4446	2290 (2497)
CBr_4	0.3112	— (2558)
CH_3I	0.5369	2577 —
CH_2I_2	0.3674	2900 (3096)
CHI_3	0.2271	3490 (3497)
CI_4	0.1450	— (3891)

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[5] R. S. Mulliken, *J. Chem. Phys.*, **8**, 234, 382 (1940).

[6] A. D. Walsh, *Quart. Revs.*, **2**, 73 (1948).

[7] K. Kimura and S. Nagakura, *Spectrochim. Acta*, **17**, 166 (1961).

[8] Mortiner J. Kamlet, "Organic Spectral Data", Vol. I, Interscience, N. Y. (1960); M. Ito, P. C. Huang and E. M. Koswer, *Trans. Faraday Soc.*, **57**, 1662 (1961).

TABLE III. OSCILLATOR STRENGTH

Compound	Calcd. by Nagakura et al.		Present	Obs.⁷⁾
	AO	non polar		
CH_3Br	0.0262	0.0422	0.0276	0.0106
CH_3I	0.0105	0.0264	0.0169	0.0087
CH_3Cl	—	—	0.0346	—

partly be ascribed to the values of the parameters adopted.

The oscillator strengths of n-σ^* transitions in bromo-methane and iodo-methane have been calculated by Kimura and Nagakura both by the VB method and by a localized molecular orbital method in which the molecular orbital is constructed in terms of two AO's of the C–X bond⁷⁾. Their results are listed in Table III for the sake of comparison. In the table, one can see that the results obtained by the VB method are much better than those by the localized molecular orbital method. In the present treatment, where the molecular orbital is delocalized, we can see that a considerable improvement in the value of oscillator strength is achieved, as is shown in the same table.

The $CH_3I \rightarrow CH_3 + I$⁶⁾ bond dissociation and the continuous absorption spectrum are observed after the light absorption takes place in these compounds.

These results might well be explained by our calculated results; that is, in the lowest vacant orbital in these compounds, electrons are localized mainly in the carbon-halogen bonds, and this orbital is strongly anti-bonding. This result is recognized in terms of the partial σ bond order* (p_{rs}) between the r-th atoms and the s-th atom in the lowest vacant orbitals of these compounds; that is, the p_{rs} values of methyl iodide are the largest among the methyl halides. These calculated values are listed in Table IV.

TABLE IV. THE CALCULATED VALUES OF PARTIAL BOND ORDER IN THE LOWEST VACANT ORBITAL OF HALOMETHANES

X	p_{C-H}	p_{C-X}
I	−0.0160	−0.7616
Br	−0.0202	−0.7504
Cl	−0.0264	−0.7370

PQR Coupling Constant.—PQR coupling constants of some halomethanes have been discussed theoretically by Hamano¹⁾. He calculated the ionic character of C–X bond by VB method. A satisfactory parallelism was observed between experimental coupling constants and his results. In the present paper, a molecular orbital procedure to discuss coupling constants is presented. We estimate the magnitude of the coupling constant by the total σ density (q_X) of halogen atoms in these compounds. Neglecting the s-character of the bonding orbital of halogen atoms, the equation connecting the coupling constant, eQq, with the total electron density, q_X, is given as⁹⁾:

$$|eQq| = (2 - q_X)|eQq_{atm}|$$

The calculated values of $|eQq|$ of some halomethanes are listed, together with the observed values¹⁰⁾, in Table V, which shows that the results obtained by our present procedure seem almost satisfactory. Hence, it may be stressed that the observed coupling constants in halomethane molecules are explained well by the magnitude of the total σ electron density.

TABLE V. THE CALCULATED AND OBSERVED VALUES OF eQq (MC) IN HALOMETHANES

Compound	Calcd.	Obs.
CH_3Cl	63.85	68.4
CH_2Cl_2	66.27	72.47
$CHCl_3$	69.56	76.98
CCl_4	74.75	81.85
CH_3Br	443.24	442
CH_2Br_2	462.67	470
$CHBr_3$	489.29	501
CBr_4	526.32	—
CH_3I	1245	1753
CH_2I_2	1321	1912
CHI_3	1401	—
CI_4	1500	2130

Proton Nuclear Magnetic Shielding in Halomethanes.—It has been pointed out that the proton chemical shift depends upon the local diamagnetic shielding, due to the electron cloud around the nucleus, and to long-range shielding due to the magnetic anisotropies of halogen and carbon atoms which are remote from the nucleus¹¹⁾. The proportion of the contribution of these two effects in propane was discussed by Narasimhan et al.¹²⁾ In the present paper, we indicate that a qualitative interpretation of the chemical shifts in halomethanes may be possible on the basis of the local diamagnetic shielding. This nuclear magnetic shielding constant in a molecule can be represented by the equation

$$\sigma_{dia} = -Aq_r \qquad \text{(in units of p. p. m.)}$$

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* This indicates the product of the molecular orbital coefficients $2C_r^jC_s^j$.

9) C. H. Towens and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

10) H. Robinson, H. G. Dehmelt and W. Gorday, ibid., **22**, 511 (1954): R. Livingston, *J. Phys. Chem.*, **57**, 496 (1953).

11) J. A. Pole, *Proc. Roy. Soc.*, **A239**, 541, 55 (1957).

12) P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, **31**, 1302 (1959).

TABLE VI. THE CALCULATED VALUES OF ELECTRON DENSITIES AT HYDROGEN ATOM AND OBSERVED CHEMICAL SHIFT IN HALOMETHANES

Compound	q_H	Chemical shift[a] (in p.p.m. from CH_4)
CH_4	0.9264	0
CH_3F	0.8912	− 7.1
CH_2F_2	0.8308	− 8.8
CHF_3	0.6948	−10.3
CH_3Cl	0.9006	− 7.1
CH_2Cl_2	0.8613	− 9.9
$CHCl_3$	0.7927	−11.8
CH_3Br	0.9058	− 7.3
CH_2Br_2	0.8784	−10.1
$CHBr_3$	0.8428	−12.4
CH_3I	0.9060	− 7.6 (−2.14)[b]
CH_2I_2	0.8808	− 9.9 (−3.85)[b]
CHI_3	0.8496	− 6.5 (−4.88)[b]

a) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).

b) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **80**, 1728 (1958).

where A is the constant and q_r is the total σ-electron density at the r-th hydrogen atom.

Hence, the resonance magnetic field of a proton is expected to increase with the total σ density. In fact, in Table VI, there exists a parallelism between the magnitude of chemical shifts and the values of the total σ density. Some further experimental investigation has been carried out on iodo-methanes and so forth. The observed chemical shifts in these molecules (written in parenthesis in Table VI) support our interpretation based upon the total σ electron density. The apparent discrepancies found in methyl fluoride, methyl chloride, methyl bromide and methyl iodide are shown to be in a reasonable order according to the values, −3.99, −2.71, −2.32 and −1.85 p. p. m. respectively, observed by Spieseck and Schneider[13]. Hence, it may be concluded that the parallelism between the observed shift and the total electron density is rather satisfactory. Regarding the quantitative interpretation, the following points should be remarked:

1. The deformation of the valence angle in these compounds is not considered.
2. The magnetic anisotropy of the neighboring atom is omitted in the present consideration.
3. The lone pair electron is considered to be thoroughly isolated in a molecule.

A further interpretation of the fluorine chemical shifts in fluoromethanes has been successfully made by the present authors; it will be published in the near future.

In the present paper, we have investigated some physico-chemical properties of halomethanes by the simple LCAO MO treatment. In spite of the extreme simplicity of our method, the calculated results are almost parallel with the observed values. If one may further adopt the modified Coulomb integrals of halogen atoms, a more comprehensive explanation of the physico-chemical properties of saturated and unsaturated σ-electron systems may be possible in the future.

Faculty of Engineering
Kyoto University
Sakyo-ku, Kyoto

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[13] H. Spieseck and W. G. Schneider, ibid., 35, 722 (1961)..