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Photoelectron Spectra and Electronic Structure of Symmetrically *Trans*-substituted Disilylethylenes

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Dedicated to Professor Dr. L. Birkofer on the occasion of his 65th birthday

The photoelectron spectra of trans-*bis(trimethylsilyl)ethylene,* trans-*bis(trimethylsilyl)dichloroethylene and* trans-*bis(trimethylsilyl)dibromoethylene have been measured. The vertical ionization energies are assigned to valence orbital energies obtained from semiempirical methods using Koopmans' theorem. Among these methods the symmetry adapted group orbital procedure proves to be most useful. Accordingly, d orbital participation may be neglected. Satisfactory assignments to σ, π and lone pair ionizations are obtained by comparing band structures and band shifts in the spectra of homologous compounds. In particular the symmetry of the two lowest levels of the molecular cations has been definitely determined which was known until now only tentatively.*

Introduction

The effect of silyl substituents on the electronic structure of unsaturated hydrocarbons was investigated already by Seidl and Bock [1, 2]. They measured the ionization energies of silyl substituted ethylenes by identifying corresponding cations from mass spectrometry and discussed the d orbital participation and inductive effects of silyl groups on the π-electron system. In all cases ionization from π molecular orbital has been assumed, although intensity relations of ultraviolet spectra [3, 4] and electron spin resonance [5] measurements of corresponding negative ions rather support σ bond properties for the highest occupied orbital and π bond characteristics for the lowest unoccupied molecular orbital. Semiempirical calculations performed for molecules like trimethylsilylethylene and trimethylallylsilanes also attributed σ symmetry to the highest orbital [6, 7]. Nevertheless, also these authors in their interpretation of photoelectron spectra assigned π symmetry to the lowest cation states and therefore when applying Koopmans' theorem [8] (although it is strictly valid only for accurate Hartree–Fock calculations) π bond characteristic to the highest occupied orbitals in these molecules.

In the present paper we would like to contribute to this discussion by investigating the photoelectron spectra of a series of homologous compounds of high symmetry for which theory allows a simple interpretation of the measured bands. It is believed that the shifts of corresponding photoelectron bands of *trans*-bis(trimethylsilyl)-, *trans*-bis(trimethylsilyl)dichloro-, and *trans*-bis(trimethylsilyl)dibromoethylene together with semiempirical calculations of different approximation will solve some of the questions concerning the assignment of bands and the electronic structure of the molecular cations. Since these molecules are planar except for the methyl groups one is able to distinguish well between σ and π energy levels.

Experimental

Synthesis of compounds

The mono- and di-Grignard compound of acetylene was reacted with chlorotrimethylsilane [9, 10]. Direct halogen addition to bis(trimethylsilyl)acetylene leading to *trans*-dihalogeno-bis(trimethylsilyl)-ethylene gave much better yields than procedures described earlier in the literature [10, 11]. Also the original synthesis [2, 12] of the *trans*-bis(trimethylsilyl)ethylene has been improved by applying the addition reaction of trimethylsilylacetylene with chlorodimethylsilane which is followed by a methyl substitution of the last chlorine by Grignard reagent. For details it is referred to a forthcoming paper [13]. All compounds were checked to be sufficiently pure by elemental analysis, i.r. and u.v. spectroscopic data and gas chromatography.

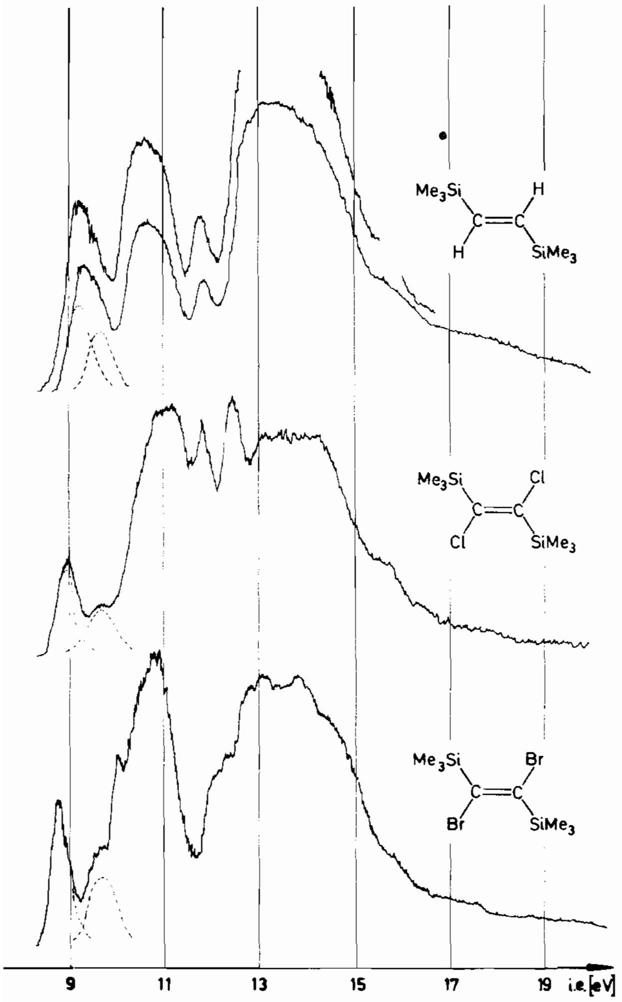

Figure 1. Photoelectron spectra of bis(trimethylsilyl)-, bis(trimethylsilyl)dichloro-, and bis(trimethylsilyl)dibromoethylene.

Spectra

Photoelectron spectra were recorded on a Perkin–Elmer PS 16 spectrometer using a He I (584Å) source. The instrument was calibrated with argon and the resolution obtained was 35–40meV.

Calculations

CNDO and extended Hückel calculations were performed on the Cyber 76 computer at the University of Cologne using the remote job entry facilities at the University of Düsseldorf.

Results and Discussion

In Figure 1 the photoelectron spectra of the three investigated compounds are presented. The low energy bands of the simplest compound ($Me_3Si–CH{=}CH–SiMe_3$) clearly shows two ionizations almost superimposed which are well separated in the spectra of the halogen homologues. This is confirmed by measuring the integral intensities of these bands if roughly equal transition probabilities for all one-electron ionizations are assumed [14–17].

We have performed a series of semiempirical molecular orbital calculations for neutral molecules using different procedures such as extended Hückel theory (EHMO), CNDO/2 [18], modified CNDO/2 according to Jaffé *et al.* [19] and Fuss [20, 21] including and not including d atomic orbital participation at Si and Cl. In all cases the highest occupied molecular orbital has σ bond character and is localized predominantly at the ethylene carbon–silicon bond moiety ($\sigma_{C–Si}$). A modified CNDO/2 calculation with more reduced π overlap parameters leads to almost equal σ and π energies for the two highest occupied orbitals (*i.e.* $10a_g$ and $6a_u$ in Fig. 2). A reversed orbital sequence is obtained from a modified CNDO/2 calculation with the original overlap parametrization except for reducing the Coulomb integral for the 3p orbital of silicon to the value of $\alpha_{3p(Si)} = -6eV$.

From a comparison of the three spectra (Figure 1) it is concluded that the first ionization must have π symmetry. This is evident from the steep ascent at the low energy side of the first bands in all spectra which is characteristic for all π ionizations due to the fact that the electrons originate from a more weakly bonded orbital relative to others. Clearly, the first ionization shifts to lower energy on substitution with chlorine and bromine, while the second one stays more or less constant. This indicates an increased mesomeric π electron effect on the first band due to mixing of halogen orbitals into the carbon π electron system [22, 23]. On the other hand the inductive effect of the halogens which should stabilize the $\sigma_{C–Si}$ bond orbitals is rather small. Furthermore the first band in the spectrum of the bromo compound exhibits a vibrational structure which is similar to that of ethylene. A four term progression with a fundamental vibration $\nu_0 = 1075\ cm^{-1}$ can be detected which compares well with the stretching frequency obtained for the ethylene cation $\nu_0^{C=C} = 1230\ cm^{-1}$ [24]. The observed decrease of 155 cm^{-1} is explained by the change in the reduced masses which are appreciably increased by the trimethylsilyl and bromo substituents. All these findings strongly support assignment of π-symmetry to the ground states of these cations.

If the molecular cation ground state is determined to be 9.2eV higher than the ground state of the neutral molecule, the other π states of the ionized species can be identified by applying theoretical methods which use molecular orbital parameters of other molecules. The first ionizations of tetramethylsilane and ethylene which are considered as molecular fragments of bis(trimethylsilyl)ethylene are 10.5eV

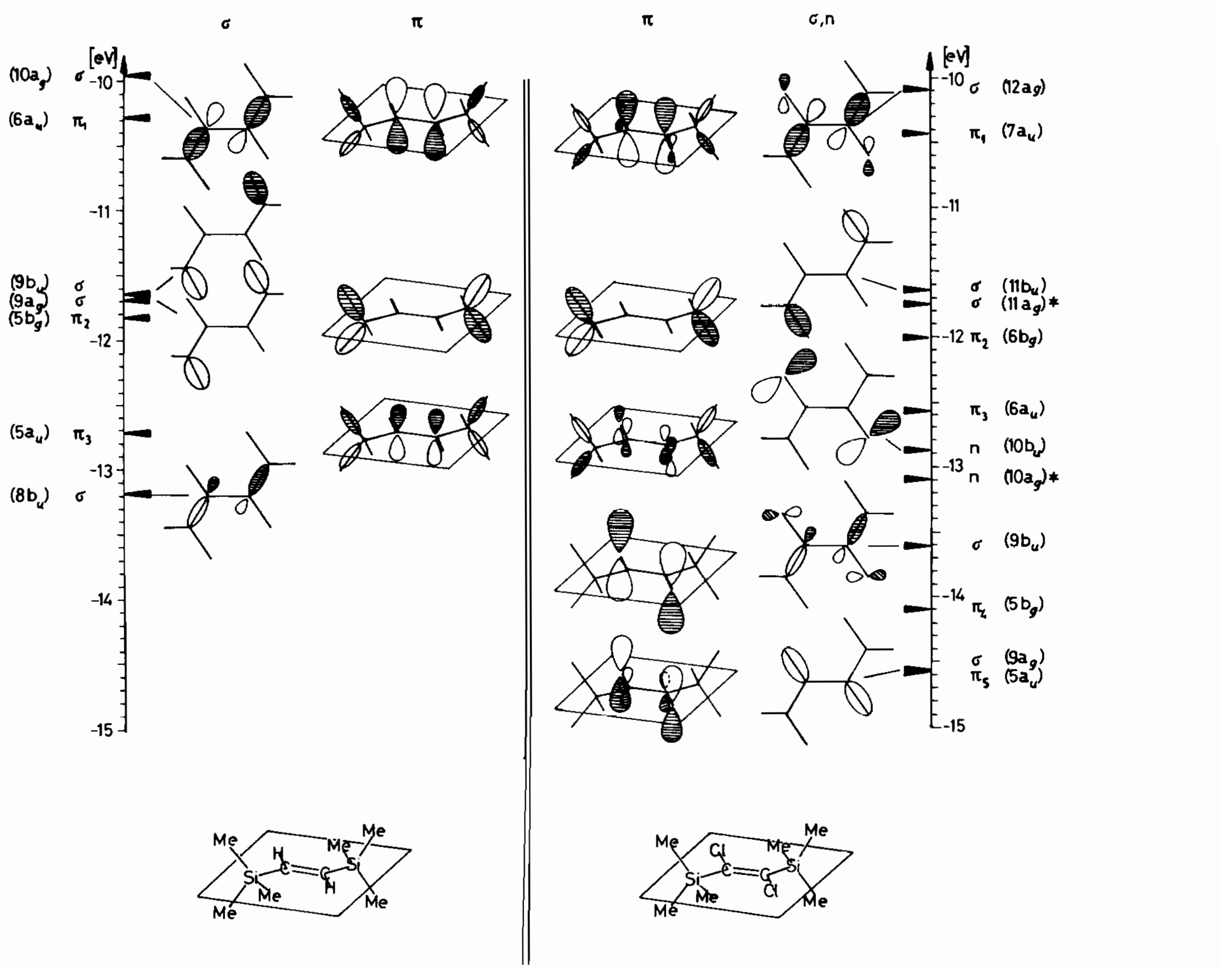

Figure 2. Orbital energies and C_{2h} group notations of the highest occupied molecular orbitals of neutral molecules as obtained from a modified CNDO/2 calculation using the usual parametrization [19–21].

TABLE I. Vertical Ionization Energies (eV) and Relative Integral Intensities (in brackets) in the Photoelectron Spectrum of *Trans*-disubstituted Silylethylenes $Me_3SiCX{=}CXSiMe_3$.

Peak No.	X = H	Cl	Br
1	9.19(1)	8.96(1)	8.83(1)
2	9.45(0.9)	9.75(0.8)	9.75(0.7)
3			10.0 (~1)
4	10.5 (3.5)	11.2 (~5)	10.9 (~5)
5	11.7 (0.8)		
6	•	11.8 (~2)	
7		12.45(1)	12.3 (~2)
8	13.6 (~14)	13.55(~15)	13.75(~15)

and 10.51 eV, respectively [24, 25]. In the symmetry adapted group orbital method [26] these energy values are transferred to the more complex molecule and are taken as orbital energies for the non-interacting system. From a combination of molecular bond orbitals of three of these fragments building up the larger molecule, π molecular orbital energies of -9.2, -10.5 and -11.8eV are calculated if no interaction is assumed between the two trimethylsilyl groups being 4.5Å apart [27]. The resonance energy representing the hyperconjugative effect of the trimethylsilyl groups on the π electron system of ethylene becomes (neglecting differential overlap) $-10.5 + 9.2 = -1.3$eV [28]. The relevant resonance integral in the Hückel type calculation is $-1.3/\sqrt{2}$ eV. If we assume that Koopmans' theorem is valid although the calculated orbitals do not arrive at Hartree Fock quality, the corresponding ionizations in the photoelectron spectrum are expected at positions given by the molecular orbital energies. Indeed, three peaks are found in the spectrum of the disilylethylene compound which are denoted in Table I by peak no. 1, 4 and 5. The band at 10.5eV is very broad with a

TABLE II. Coulomb Integrals α, Resonance Integrals β, and Inductive Shift Parameters $\Delta\alpha$ of π Ethylene in eV Obtained from Relevant Photoelectron Spectra Which Are Used for the Group Orbital Calculation (taken partly from ref. 23).

Y	α_Y	$\beta_{Y,C=C}$	$\Delta\alpha_{C=C}$
$SiMe_3$	−10.5	−0.92	0
Cl	−12.6	−1.27	−0.22[a]
Br	−11.6	−1.13	−0.19[a]
C=C	−10.5		

[a] Parameter per halogen atom.

relative intensity of 3.5 indicating a superposition of about 4 ionizations. However, the band at 11.7 (peak no. 5) is isolated and rather sharp which is a good evidence for an ionization originating from a π orbital.

The satisfactory agreement between the theoretical model considering only π orbitals and the experiment allows for a criticism of the modified CNDO/2 calculations which may give an indication in which way the calculations must be corrected in order to give better results also for other types of ionizations as those from σ bonds and lone pair electrons n_X. As pointed out by Mollère [29] the calculated (by modified CNDO/2 [19–21]) and measured σ and π cation states of methyl- and silylethylenes correlate almost linearly to each other. This relation is, however, different for σ- and π-orbitals reflecting correct orbital energy sequences within σ- and π-series, respectively. The corresponding energy intervals differ between theory and experiment only by different scaling factors. For the modified CNDO/2 calculation these linear dependencies for the σ and π orbital series are very similar which also is an improvement over calculations performed by the original CNDO/2 method [18]. Therefore, the comparison with experimental results indicates that the order of the highest occupied $\sigma(10a_g)$ and $\pi(6a_u)$ orbitals as calculated from semiempirical methods with usual parametrization may be reversed compared to that in the experiment. For the same reason the order of the two calculated orbitals $5a_u(\pi)$ and $8b_u(\sigma)$ at about 10.7eV may be changed as is suggested also by relative intensity arguments: the calculated intensities as obtained from the number of orbitals within various regions in the orbital scheme give intensity ratios of 2:3:2:15 (Figure 2) which are compared with the experimentally measured relative intensities of about 1.9:3.5:0.8:14 (see Table I). A smaller σ orbital splitting of $10a_g$ and $8b_u$ may correct the calculated relations in the second and third orbital energy region yielding the experimental relation as given in the peaks no. 4 and 5 of Table I. A decreased π overlap integral between the two ethylene carbon atoms which is smaller than the corresponding parameter in the modified CNDO/2 is not able to reproduce the correct grouping of the orbitals. However, if the Coulomb integral of the silicon p orbital is allowed to accept values of around $\alpha_{3p(Si)} = -6$eV the modified CNDO/2 procedure with its original parametrization is able to reduce the σ orbital splitting so much that it explains the experimentally found intensity relation 2:4:1 for the first three orbital regions. This parameter choice shows a better general agreement of calculated and experimental data.

TABLE III. Theoretical and Experimentally Found Ionizations (in eV) for $Me_3Si{-}CX{=}CX{-}SiMe_3$ Omitting All σ Ionizations Which Belong to $Me_3Si{-}CH{=}CH{-}SiMe_3$

	Theoretical			Experimental
	π (Calculated)	n_X (Obtained from XCH=CHX)	σ_{C-X} (Obtained from XCH=CHX)	
X = Cl	9.0			8.96
	10.5			10.5
	11.2			11.2
		11.8		
		12.0		11.9
	12.6			12.5
	13.9		14.5	~14
X = Br	8.9			8.83
	10.5			
	10.9	11.0 (2×)		10.7 (2×)
	11.6			11.9 (2×)
	13.1		13.3	~13

For a band assignment of the halogen derivatives we use the results obtained for the unsubstituted silylethylene. In particular the resonance integral $\beta_{SiMe_3, C=C} = 1.3/\sqrt{2} = -0.92$eV between the symmetric group orbitals of the Me_3Si radical and the π orbital of ethylene is assumed to be transferable to the halogen compounds. The other parameters which are necessary for a calculation by the group overlap method are taken from the photoelectron spectrum of the dihalogenoethylenes [23]. The parameter set is compiled in Table II. The expected photoelectron bands obtained from the orbital energies using Koopmans' theorem are listed in Table III. A comparison with the experiment shows that the 9.0, 11.2 and 12.6eV bands for the chloro compound and the bands at 8.9 and 10.9eV for the bromo compound can be easily assigned to corresponding bands in the experimental spectra since these regions are not superimposed by other ionizations. In order to detect the π bands hidden under the σ bands we may deduct these σ bands which we may construct from the spectrum of the unsubstituted compound as described below. This procedure assumes, of course, that the σ framework of $Me_3Si{-}C{=}C{-}SiMe_3$ is not changed appreciably on halogen substitution. The results from a modified CNDO/2 calculation justify

TABLE IV. Assignment of All Vertical Ionization Energies $i.e_v$. in the Photoelectron Spectrum of $Me_3Si{-}CX{=}CX{-}SiMe_3$ to Bond Orbitals of Point Symmetry C_{2h} and Main σ and π Bond Characteristics as well as Lone Pair Electrons n_X .

X = H			Cl			Br		
$I.e_v$. (eV)	Orbital Symmetry	Bond Charact.	$I.e_v$. (eV)	Orbital Symmetry	Bond Charact.	$I.e_v$. (eV)	Orbital Symmetry	Bond Charact.
9.19	$6a_u$	π_1	8.96	$7a_u$	π_1	8.83	$7a_u$	π_1
9.45	$10a_g$	$\sigma_{Si-C=}$	9.75	$12a_g$	$\sigma_{Si-C=}$	8.75	$12a_g$	$\sigma_{Si-C=}$
						10.0	$11b_u$	n_{Br}
10.4	$9b_u$	σ_{Si-CH_3}	10.4	$11b_u$	σ_{Si-CH_3}	10.4	$10b_u$	σ_{Si-CH_3}
10.4	$9a_g$		10.4	$11a_g$		10.4	$11a_g$	
10.5	$5b_g$	π_2	10.5	$6b_g$	π_2	10.5	$6b_g$	π_2
10.8	$8b_u$	$\sigma_{Si-C=}$	10.8	$9b_u$	$\sigma_{Si-C=}$	10.8	$9b_u$	$\sigma_{Si-C=}$
11.69	$5a_u$	π_3	11.2	$6a_u$	π_3	10.8	$6a_u$	π_3
			11.8	$10b_u$	n_{Cl}	11.7	$5b_g$	π_4
			12.0	$10a_g$		12.1	$10a_g$	n_{Br}
			12.5	$5b_g$	π_4			
			14.0	$5a_u$	π_5	13.2	$5a_u$	π_5
			14.5	$9a_g$	σ_{C-Cl}	13.3	$9a_g$	σ_{C-Br}
12 - 15		σ_{C-H}	12 - 15		σ_{C-H}	12–15		σ_{C-H}

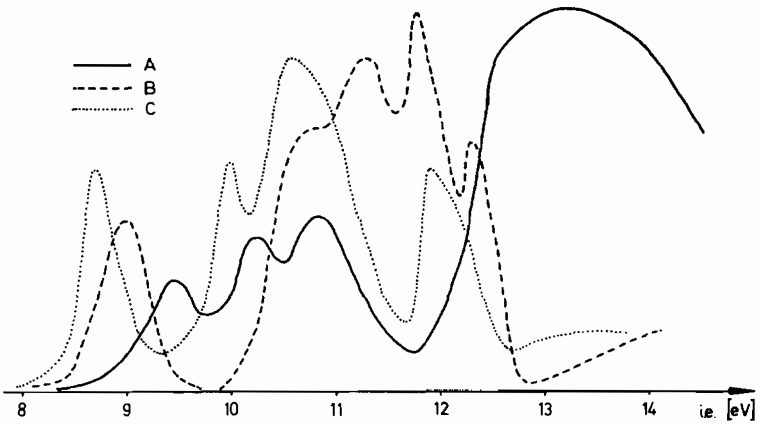

Figure 3. Difference spectra. (A) The measured spectrum of $Me_3SiCH{=}CHSiMe_3$ minus three π ionizations (see text), (B) the measured spectrum of $Me_3SiCCl{=}CClSiMe_3$ minus spectrum A, (C) the measured spectrum of $Me_3SiCBr{=}CBrSiMe_3$ minus spectrum A.

this assumption to a great extent. The deduction proceeds as follows. From the measured spectrum of the unsubstituted compound (Figure 1) the positions and shapes (calculated Lorentz curves [30] from experimental integral intensities) of the π ionizations at 9.2, 10.5 and 11.7eV are deducted yielding the spectrum for the σ framework $Me_3Si{-}C{=}C{-}SiMe_3$ (spectrum A of Figure 3). The resulting spectrum is subsequently deducted from the experimental spectra of the chloro and bromo compounds leading to the spectra B and C in Figure 3. These spectra should contain all π ionizations, the lone pair ionizations n_X of the halogens and those σ ionizations which are localized predominantly in the carbon–halogen bond. One should keep in mind that on halogen substitution there will be one carbon–hydrogen bond removed which is observed, however, only at higher energy in the spectrum [23]. The difference spectra confirm the peaks of calculated π ionizations and the expected halogen lone pair bands in a satisfactory way. The lone pair ionizations for the chlorine derivative compare well with those obtained for dichloroethylene [23]. The assignment of the very steep 10.0 and 12.2eV band of the bromine compound to lone pair ionization is derived from the structure of these bands; this is also suggested by the fact that no other transitions are available from theory. These bands have, however, no correlates in dibromoethylene. The ionizations of the carbon halogen σ-bond orbital which are expected at 14.5eV for the chlorine and at 13.3eV for the bromine derivative [23] cannot be determined accurately since in this region the deductive procedure does not work properly any more due to the necessary omissions to be made.

The results of the present discussion are summarized in Table IV where all assignments and bonding characteristics for the three compounds investigated are compiled. The low ionization energy of the σ_{C-Si} bond is an indication for the small bond strength which is manifested by the high mobility of methylsilyl groups in larger molecules such as pyrazolines, which is comparable to the migration rate of hydrogen [13].

Conclusions

A satisfactory assignement of photoelectron bands to valence bond orbitals can be obtained by comparing the spectra of homologous compounds. Band shapes, vibrational structures and band shifts in the spectra of similar compounds are relevant guides for determining corresponding oribtal energy schemes by the use of Koopmans' theorem. The most useful assistance for this attempt, however, is provided by symmetry adapted group orbital calculations [26] which prove to be superior to other semiempirical theories although they do not obtain the Hartree–Fock quality. Only the modified CNDO/2 procedure [19–21] with a parametrization partially different from the usual one is able to reproduce the actual orbital sequences characterized by σ and π symmetry. From the apparent success of the group orbital method when applied to a series of molecular homologues it is concluded that certain Coulomb and resonance energy parameters can be transferred without changes from one molecule to another. The fact that Koopmans' theorem obviously can be applied if only very approximate orbital energies are calculated shows that the accurate Hartree–Fock orbitals are determined mainly by symmetry properties which they have in common with semiempirical (self consistent) orbitals. Higher orbitals, *e.g.* unoccupied d orbitals at Si or Cl, do not seem to contribute very much to the stability of cationic states.

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