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PHOTOELECTRON SPECTRA OF IODO ETHYLENES[1-3]

A SIMPLE METHOD TO INCORPORATE SPIN ORBIT COUPLING IN MOLECULAR ORBITAL MODELS

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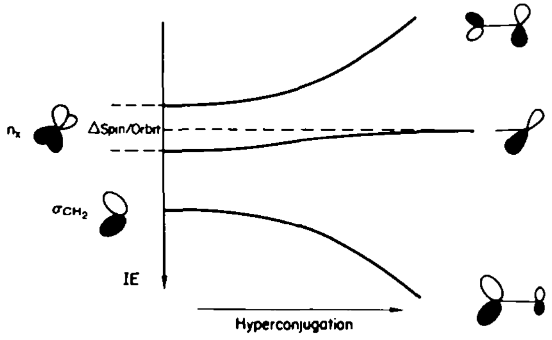
Abstract—Spin orbit interactions can no longer be neglected in MO-models for molecules with heavy atoms. For qualitative discussions double group representations prove useful. In semi-empirical calculations as e.g. the Extended Hückel approximation atomic spin orbitals may be used in the basis set. The molecular spin orbitals obtained display the required symmetry properties and their eigenvalues correspond satisfactorily to the ionization potentials determined by photoelectron spectroscopy.

Zusammenfassung—Spin Bahn-Kopplung kann in MO-Modellen für Moleküle mit schweren Atomen nicht länger vernachlässigt werden. Qualitativ läßt sie sich über die Darstellungen der Doppelgruppen berücksichtigen. In semiempirischen Rechenverfahren wie der Extended Hückel-Näherung können atomare Spinorbitale im Basissatz verwendet werden. Die erhaltenen Molekül-Spinorbitale haben die geforderten Symmetrieeigenschaften und ihre Eigenwerte stimmen befriedigend mit den photoelektronenspektroskopischen Ionisierungsenergien überein.

Introductory remarks

Photoelectron (PE) spectroscopy has furnished experimental evidence for many qualitative concepts used in molecular orbital models.[4-6] Molecular orbitals and their energies evade exact experimental determination, only electron densities or differences in total energies of molecular states can be measured. However, via Koopmans' Theorem[5] orbital energies obtain some physical significance.

There is a nearly complete symbiosis between MO-models and PE spectroscopy; even finer details such as vibrational fine structure or Jahn Teller distortions can be rationalized.[5] Spin orbit interactions, however important they are for all heavier elements, nevertheless are barely understood except in some simple cases.[4,7,8] In particular, degenerate electron pairs of heavy atoms are split by spin orbit coupling, e.g. in hydrogen iodide by 0·66 eV.[9] In all molecules without main rotational axis C_n of order $n \geqslant 3$ to the observed splitting other interactions may contribute, e.g. hyperconjugation, as explicitly discussed by Brogli and Heilbronner.[8] With increasing hyperconjugation the spin orbit contribution to the experimentally observed splitting is reduced. Any partitioning has to rely on calculations, which are the more necessary the greater the number of interactions which have to be considered.



(1)

Molecular spin orbitals

The MO-concept can easily be extended to molecules with substantial spin orbit coupling.[10] This interaction is approximated by an one-electron

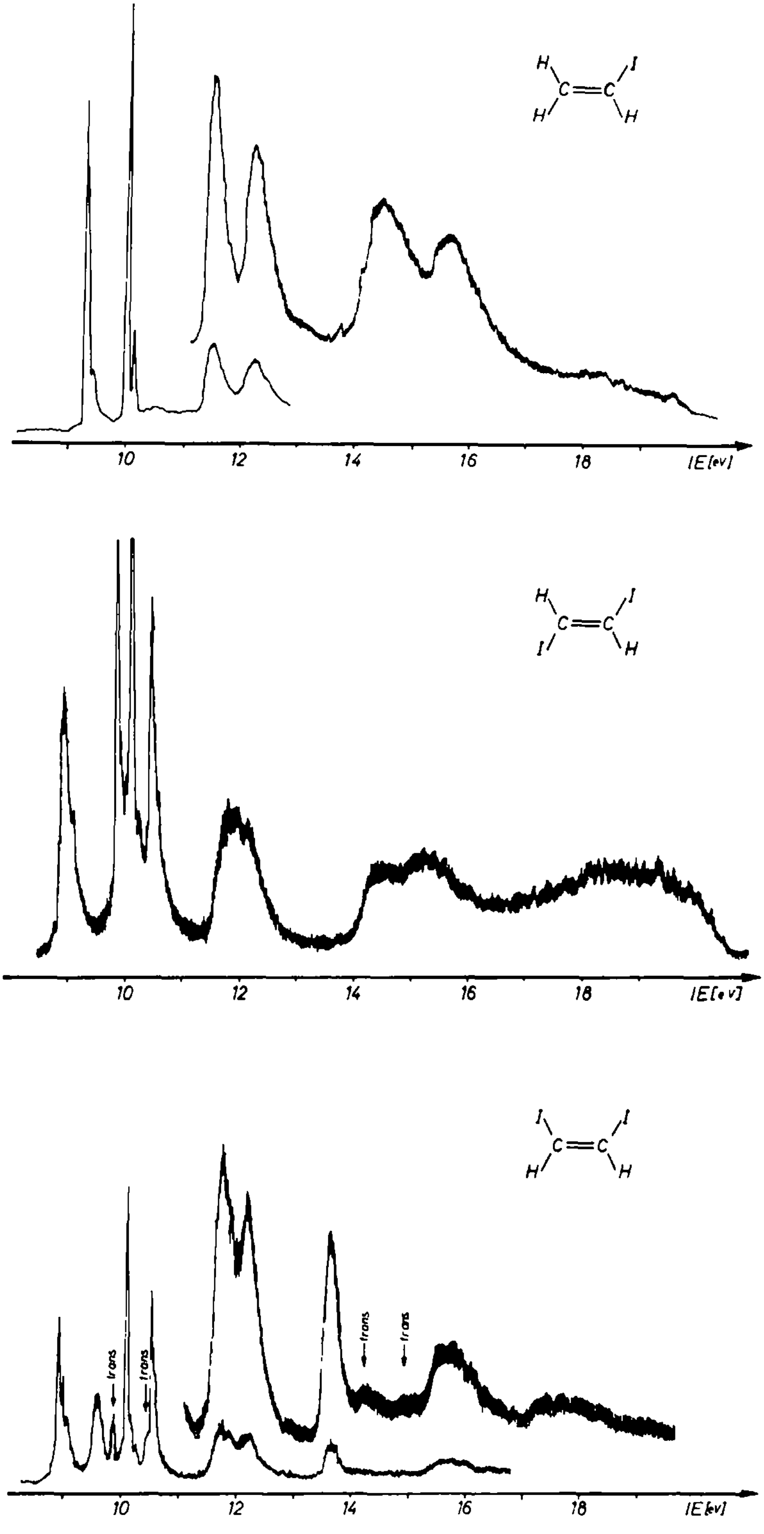


Fig 1. Photoelectron spectra of vinyliodide, *cis*-, and *trans*-diiodoethylene.

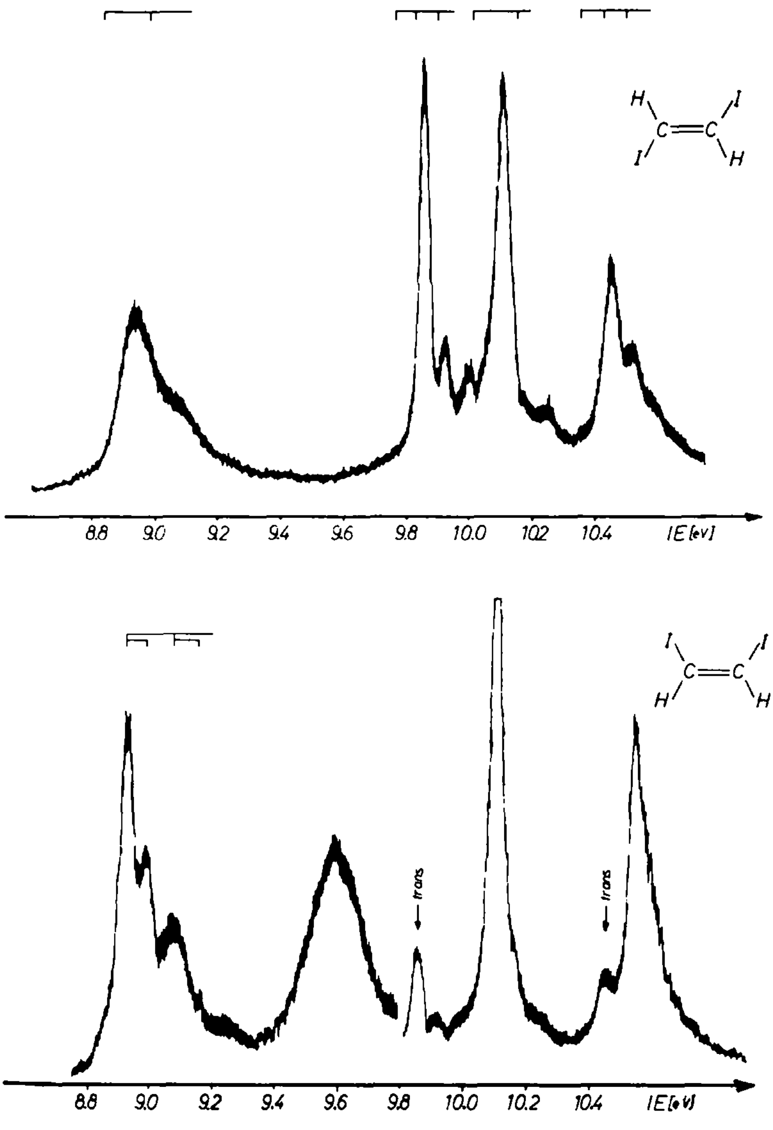


Fig 2. Expanded records of the PE-spectra of the 1·2 diiodoethylene.

operator*

$$h_{\text{spin/orbit}} = \sum_{A} \zeta_A \cdot \vec{l}_A \cdot \vec{s} \qquad (2)$$

where the summation runs over all nuclei A, where $\vec{l}$ and $\vec{s}$ are the orbital and spin angular momentum operators, and where ζ_A is the spin orbit coupling constant, taken from the spectra of atomic cations.[11]

Normally, without spin orbit interaction, the effective one electron operator H_{eff} is diagonalized in a basis of atomic orbitals. The resulting eigenvalues are the orbital energies, and the eigenvectors are the molecular orbitals. To the normal operator

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[*] The one center matrix elements of $h_{\text{spin/orbit}}$ are evaluated in the usual way.[a] In the EHMO-procedure, Slater type orbitals are used. The two and three center matrix elements are neglected except the one which is approximated[10] by

$$\langle \phi_i^A | \zeta_A \vec{l} \cdot \vec{s} | \phi_j^B \rangle = \sum_{k \text{ on } A} \langle \phi_i^A | \vec{l}_A \cdot \vec{s} | \phi_k^A \rangle \cdot \langle \phi_k^A | \phi_j^A \rangle \cdot W \cdot \zeta_A$$

The expansion includes all the valence orbitals on A only. The constant W allows for greater flexibility and was given the value W = 0·4[10] by fitting experimental and calculated spin orbit splittings of small molecules.

[a] E. U. Condon and G. H. Shortely, *The Theory of Atomic Spectra*, Cambridge University Press (1935).

$H^{\bullet}_{eff}$, which contains kinetic energy terms as well as the electrostatic interactions among the electrons and the nuclei, the spin orbit operator is added (3).

$$H_{eff} = H^{\bullet}_{eff} + h_{spin/orbit} \qquad (3)$$

The resulting operator H_{eff} is then diagonalized in a basis of atomic spin orbitals: Each atomic orbital has to be doubly included, one with α, one with β spin, since the spin orbit operator (2) depends on spin. The diagonalization now yields molecular spin orbitals and molecular spin orbital energies.

This approach, like ordinary SCF-calculations, has the advantage that cationic states and molecular spin orbitals have the same symmetry properties. Thus the familiar Koopmans' theorem can be applied directly.

The spin functions α and β have a rather peculiar property: Each is converted into its negative by a full rotation of 2π.[12a] This rotation is therefore different from the identity operator and is added to the molecular point groups as an extra generating element. These enlarged groups are called double groups.[12b] The molecular spin orbitals transform as the irreducible representations of the double groups, their species are obtained in the usual way as direct products of the species of the molecular orbitals and of the spin functions. The latter transform according to $e_{1/2(g)}$.[12b] It should be noted, that σ and π spin orbitals may have the same species in the double group, for instance in C'_{2h}:

$$\begin{aligned} a_u \times e_{1/2g} &= e_{1/2u} \\ b_u \times e_{1/2g} &= e_{1/2u} \end{aligned} \qquad (4)$$

The MO-procedure actually used is of the Extended Hückel type.[10] This simplest σ/π-approximation was preferred to more sophisticated ones, because it is easy to parametrize, and its results are more readily analysed. Nevertheless, as will be shown in the subsequent section, there is a satisfactory reproduction of the measured PE ionization potentials.

Example: The PE spectra of iodo ethylenes and their interpretation using molecular spin orbitals

The PE-spectra of vinyliodide, *cis*- and *trans*-1,2-diiodoethylenes are presented in Fig 1, their vertical ionization potentials are summarized in Table 1. Details of some bands are shown in Fig 2, observed vibrational frequencies of cation states are listed in Table 2.

In order to facilitate the discussion of the PE spectra a qualitative MO scheme should demonstrate the forming of the molecular spin orbitals for *trans*-diiodoethylene (Fig 3).

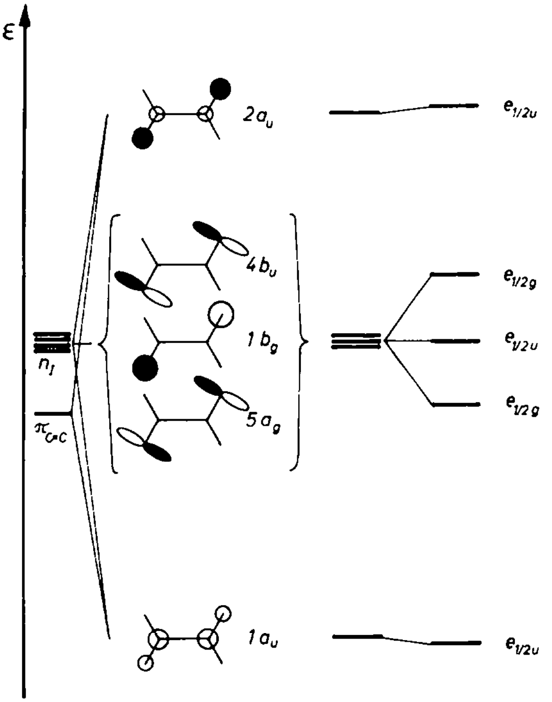

Fig 3. Qualitative MO scheme for the five highest occupied levels of *trans*-diiodoethylene.

Spin orbit coupling mixes mainly the nearly degenerate iodine lone pair orbitals $5a_g$ and $1b_g$, both belonging to the $e_{1/2g}$ representation within the double group C'_{2h}. The ungerade orbitals $2a_u$, $4b_u$ and $1a_u$ (C'_{2h}: $e_{1/2u}$) are only slightly perturbed due to their large energy difference.

The PE spectrum of *trans*-diiodoethylene is readily assigned on the basis of the above discussion: Arising from two strongly coupled lone pairs, the splitting of the two $e_{1/2g}$ molecular spin orbitals should not be less than 0·6 eV, the atomic coupling constant of iodine (exact value 0·628 eV[11]). There is only one group of PE bands within a 0·6 eV range (Figs 1 and 2), which establishes the orbital sequence (Fig 3) for the five lowest ionisation potentials (Table 1: ① to ⑤).* The remaining four bands are assigned according to EHMO calculations (Fig 4).

The above simple MO arguments cannot be extended to the *cis*-isomer because all states belong to the same irreducible representation, i.e. $e_{1/2}$ in C'_{2v} (Table 3)

Although the PE assignments of *cis*-diiodoethylene and of vinyliodide as well are reduced to the triviality of simply numbering the states, the chemist is more interested in the extent of spin orbit interaction. Being a rather artificial subdivision, nevertheless, only an estimate of this effect allows comparison with other molecules, where spin orbit interaction is too small to be observed in the PE-spectra. Therefore Extended

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*By the same argument, in *trans*-dibromoethylene, the $5a_g$ and $1b_g$ levels cannot be degenerate as was assigned previously[13].

Table 1. Vertical ionization potentials IP_n (eV)

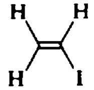
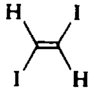
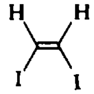
	①	②	③	④	⑤	⑥	⑦	⑧	⑨
	9·35	10·08	11·55	12·25	14·5	15·6	(18·3)		
	8·92	9·86	10·11	10·45	11·85	12·15	14·4	15·3	(18·3)
	8·94	9·60	10·11	10·55	11·75	12·20	13·65	15·65	(17·5)

Table 2. Vibrational fine structures ν^+ (cm^{-1})

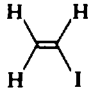
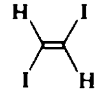
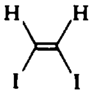
						
①	②	①	②	③	④	①
320 1140	1050	960	560	920	560	480 1250

Table 3. Symmetry species of lone pair and ethylene π-orbitals in the point and double groups (indicated by a prime)

	C_2H_3I		*trans* $C_2H_2I_2$		*cis* $C_2H_2I_2$	
	C_s	C'_s	C_{2h}	C'_{2h}	C_{2v}	C'_{2v}
$\pi_{C=C}$	a''	$e_{1/2}$	a_u	$e_{1/2u}$	b_1	$e_{1/2}$
n_π	a''	$e_{1/2}$	a_u	$e_{1/2u}$	b_1	$e_{1/2}$
			b_g	$e_{1/2g}$	a_2	$e_{1/2}$
n_σ	a'	$e_{1/2}$	a_g	$e_{1/2g}$	a_1	$e_{1/2}$
			b_u	$e_{1/2u}$	b_2	$e_{1/2}$

Hückel calculations with[10] and without inclusion of spin orbit coupling have been carried out, the results of which are displayed in Fig 4.

Some points need further comment: Normal Extended Hückel calculations yield the ethylene π orbital too close to the σ orbitals. This was taken into account by adding an extra 1·7 eV to the carbon $2p_\pi$-parameter. This parametrization is well balanced, comparing the relative energies of C—H and C—I bonding and iodine lone pair orbitals. No further attempt was made to achieve better agreement between calculated and experimental ionization potentials. Thus in *cis* - diiodoethylene, the Extended Hückel calculation yields $4b_2$ above $2b_1$. From experience with other haloethylenes[2,3,14] it might be argued that this sequence is wrong: The shape of the 9·60 eV band is typical for the $4b_2$ ionization in the other *cis*- and 1,1-dihaloethylenes.[14] Furthermore, no definite assignment can be made for the two adjacent bands near 12 eV in all compounds. Comparison with other haloethylenes[14] favours the assignment, IE(π) < IE (σ_{C-I}).

The numbers in Fig 4 represent the effect of spin orbit interaction. In vinyliodide the difference of the first two ionization potentials (Table 1: 0·73 eV) is of the same magnitude as the atomic coupling constant of iodine. According to the calculations the spin orbit contribution to the splitting dominates the π-conjugation as is also reflected by the sharpness of the first two peaks. Based on simple Hückel argument the π interaction should increase by a factor $\sqrt{2}$ in the diiodo compounds, therefore a reduced spin orbit contribution for the first ionization potential is calculated. In the *cis*-isomer, where all spin orbitals are of the same symmetry $e_{1/2}$ (Table 3), the lone pair orbitals mix considerably and hardly any correlation seems possible with the starting molecular orbitals. Due to its favourable symmetry (Table 3), for *trans*-diiodoethylene such

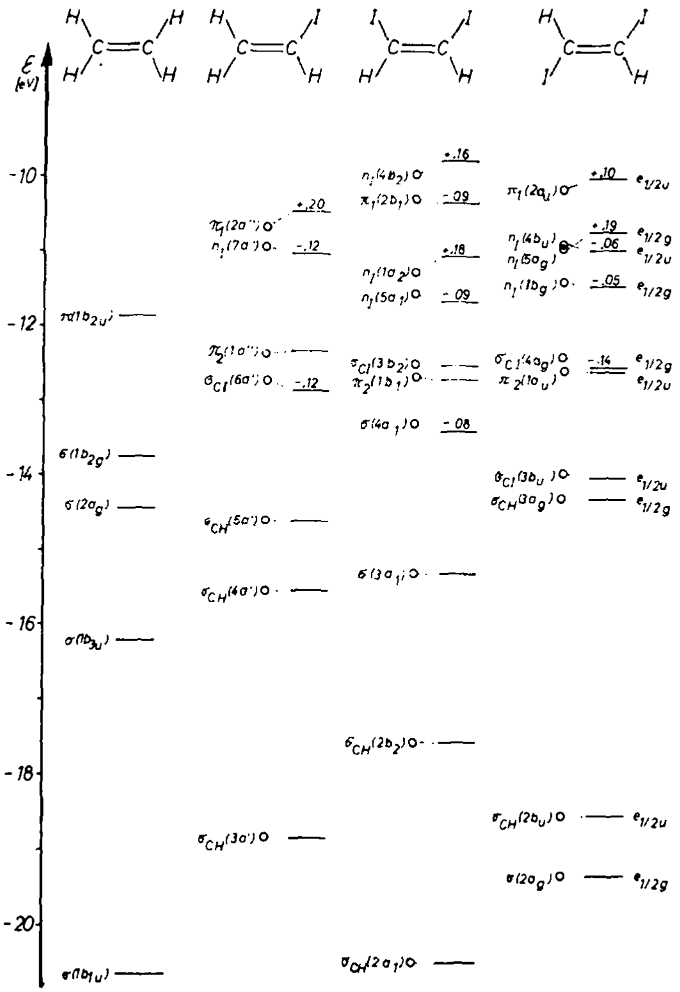


Fig 4. Spin orbital energies (--) and orbital energies (0) for iodoethylenes. (Numbers are differences between the two types of calculations).

a classification can be obtained (Fig 3). It should be pointed out, that only inclusion of spin orbit coupling reverses the sequence of the g and u levels in the lone pair region and yields the correct orbital sequence, in full accordance with the PE assignment of all other halo - ethylenes investigated[14] and the perturbation arguments displayed in Fig 3.

As expected,[10] there is hardly any spin orbit interaction in the σ bonding orbitals: these can therefore be labeled by the irreducible representations of the simple point groups (Fig 4). The assignments for the σ-orbitals are based on Extended Hückel calculations and the correlation with the ethylene PE spectrum. The orbital sequence is more or less determined by the C—H bonding contributions and the Extended Hückel calculations seem to be rather reliable in this σ region. Thus for the vinyliodide, *cis*- and *trans*-diiodoethylene the orbitals 6á, $3b_2$ and $4a_g$ are predicted at nearly equal energies, in good agreement with the PE spectra. Finally the varying differences IE(8) − IE(7), significant for the *cis*/*trans* pair, are well reproduced by the Extended Hückel calculations (compare Fig 4 and Table 1).

Concluding remarks

In all three iodoethylenes discussed, spin orbit coupling plays an important rôle. Even in these simple compounds, calculations are almost required in assigning the PE spectra. In addition, they provide estimates of the competing interactions, i.e. spin orbit coupling *vs* conjugation.

PE spectra always show only the overall substituent effect. Thus one might argue from the experimental splitting patterns[15] of e.g. group IV diiodides H_2XI_2 (Fig 5) that the electronic structure is similar.

However as is evident from Fig 5, the relative importance of spin orbit coupling increases in the series C < Si < Ge. Due to the larger distance d_{I-I},

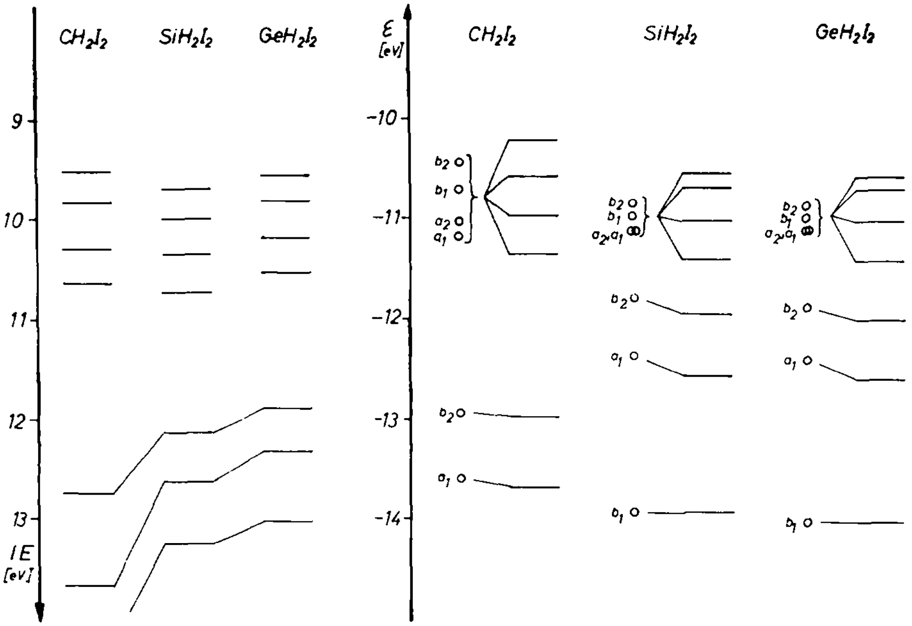


Fig 5. PE splitting patterns and their comparison with extended Hückel eigenvalues with (––) and without (O) inclusion of spin orbit coupling.

the overlap and therefore the splitting of the lone pairs decreases. Only the increasing spin orbit contribution will explain the observed similarity in the lone pair region of the H_2XI_2 PE spectra.

The general agreement between PE spectra and the calculations strongly suggest, that the calculated spin orbit contributions are especially important in the low energy region, where they sometimes dominate. In addition it is the highest occupied orbitals which determine spectral properties and in many cases chemical reactivity ("frontier orbitals").[16] The molecular spin orbital approach proposed retains all advantages of simple MO-models. Thus all the experience gathered by applying the MO language to chemical and spectroscopic problems can be transferred. The programmed Extended Hückel version is quite helpful for the discussion of less symmetric molecules, where intuitive understanding of electronic structure is often lacking.

EXPERIMENTAL

Vinyliodide was obtained from 1,2-diiodoethane by treatment with NaOH,[17] *trans*-diiodoethylene (m.p. 72°) by passing acetylene through an alcoholic solution of I_2.[18] It was isomerized at 160° in the presence of I_2; subsequent fractional crystallization yielded the eutecticum melting at $-11°$[19]. The purity of all compounds was checked by mass and PE spectroscopy, the latter being very sensitive to iodine containing compounds.

The PE spectra were taken on a Perkin Elmer PS 16 and were calibrated with argon (FWHM 25 meV).

Calculations were performed on the UNIVAC 1110 at the University of Bergen. Details of the program together with parameter set are described elsewhere.[10]

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