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THE UV GAS-PHASE PHOTOELECTRON SPECTRA OF GROUP IVB TETRAPHENYL DERIVATIVES

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Summary

The He(Iα) and He(IIα) photoelectron spectra of the $M(C_6H_5)_4$ series of molecules (M = C, Si, Ge, Sn, Pb) have been recorded and analysed on the basis of correlations with the known electronic structures of corresponding MH_4 hydrides and of benzene. Extended Hückel MO calculations were also performed for all the molecules in the series. The photoelectron spectra of the $M(C_6H_5)_4$ molecules all bear a strong resemblance to the benzene spectrum, suggesting that there are only weak interactions between the phenyl ligands.

Introduction

The study of the electronic structure of large molecules by photoelectron spectroscopy is often limited to measurements on the first few molecular orbitals, i.e. those with the lowest ionization energies. The main reason for this is that the high density of allowed ionized states in the higher ionization energies region results in broad features corresponding to ionization from several orbitals, making detailed assignments difficult. Sophisticated quantum chemical calculations are of little help in such cases because the small energy separation between ionized states makes calculated ionization energies unreliable for assignment purposes. High quality calculations for large molecular systems also tend to become prohibitively costly and time consuming. However, if a large molecule has high symmetry the energy levels are frequently grouped into several well defined subsets, thus simplifying the analysis of the spectrum and associated calculations. A good example of such a molecular system is provided by the tetraphenyl derivatives of Group IVB elements $M(C_6H_5)_4$ M = C, Si, Ge, Sn, Pb.

The crystal and molecular structures of these compounds, as well as their molecular vibrations have been studied extensively [1]. The results show that all the

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$M(C_6H_5)_4$ molecules have S_4 site symmetry in the solid state. The only gas-phase molecular structure determination reported so far deals with $Sn(C_6H_5)_4$, and indicates S_4 symmetry in the gas phase [2]. It is, therefore, reasonable to assume that other Group IVB tetraphenyls have the same symmetry in the gas phase. Molecules of the $M(C_6H_5)_4$ series have an interesting shape, in that when viewed along any of the four 'tetrahedral' bonds (i.e. bonds between central atom and phenyl rings) the three remaining rings form a propeller-like arrangement. The molecules are flexible and rotation of benzene rings around the 'tetrahedral' bonds can reduce the steric strain produced by HH non-bonding interactions.

Experimental

The He(Iα) and He(IIα) photoelectron spectra of gas phase $M(C_6H_5)_4$ M = C, Si, Ge, Sn, Pb were recorded with the molecular beam photoelectron spectrometer described previously [3]. The samples were of commercial origin (Aldrich Chem. Co., T. Schuhardt GmbH Co.) and were purified by vacuum sublimation before use.

Results and discussion

The He(Iα) and He(IIα) photoelectron spectra of the molecules studied are shown in Figs. 1 and 2 respectively. Ionization energies are given in Table 1.

It is apparent that the spectra of all five tetraphenyls are closely similar to one another, and also bear a strong resemblance to the spectrum of benzene [4] (Fig. 1).

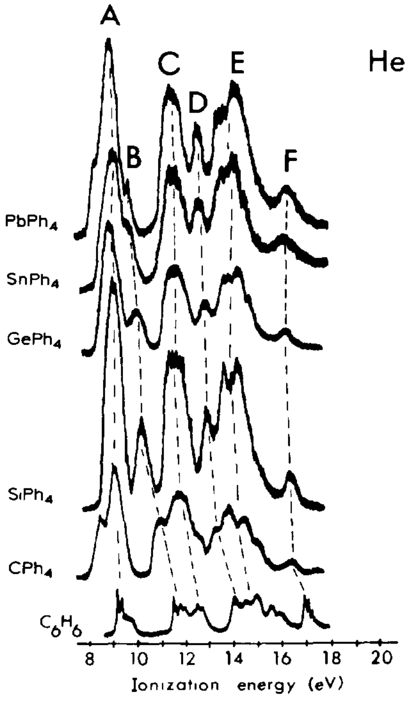

Fig. 1. He(Iα) photoelectron spectra of Group IVB tetraphenyls and benzene.

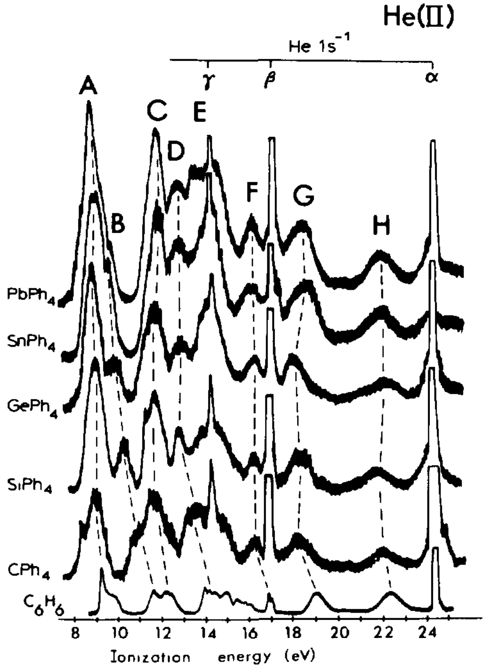

Fig. 2. He(IIα) photoelectron spectra of Group IVB tetraphenyls and benzene.

Thus feature A clearly correlates with the 9.25 eV π^{-1} ionization in benzene, while features B + C and D + E correlate with benzene features centered at 12 and 14.5 eV. A similar resemblance to the benzene spectrum is also shown by the spectrum of triphenylphosphine [5], and similarities between the photoelectron spectrum of tetravinylstannane and ethylene have recently been noted and used to make assignments of the tetravinylstannane spectrum [6]. These comments suggest that the $M(C_6H_5)_4$ spectra might be interpreted simply in terms of weak interactions between four benzene molecules. The $M(C_6H_5)_4$ and a $(C_6H_6)_4$ system would have the same number of valence electrons, but for a simple comparison to be valid the metal atom would need to provide four equivalent electrons, i.e. to provide four sp^3 hybrid orbitals. Such an approach has not previously been found to be applicable either to the Group IVB hydrides [7] or to the Group IVB tetramethyls [8]. Here metal–ligand (M–X) bonding can be described in terms of three t_2 orbitals showing marked metal p character and an a_1 orbital with substantial metal s character. The classification refers to the T_d M–X bond symmetry.

On this basis, for the $M(C_6H_5)_4$ system it is logical to look at the form of the benzene parent orbitals which might be expected to give rise to $M-C_6H_5$ bonding. These will be formed from those benzene orbitals with a substantial carbon hydrogen bonding contribution i.e. one from each of the $3e_{2g}$, $3e_{1u}$ and $3a_{1g}$ orbital combinations [9]. However, on energy grounds, bearing in mind the position of the t_2 M–X bands in MH_4 and $M(CH_3)_4$ spectra, the 11.5 eV, $3e_{2g}$ benzene orbitals are most likely to be involved in MX bonding.

On this basis, band B (Fig. 1) is assigned to ionization from the three t_2 type orbitals formed from the benzene $3e_{2g}$ orbitals. In S_4 symmetry these will be $e + b$

TABLE 1

ASSIGNMENTS AND IONIZATION ENERGIES (band maxima in eV) FOR THE PHOTOELECTRON SPECTRA OF GROUP IVB TETRAPHENYLS

Band	A	B	C	D	E	F	G	H
Benzene assignment [a]	$8 \times 1e_{1g}$	$3 \times 3e_{2g}$	$5 \times 3e_{2g} +$ $4 \times 1a_{2u}$	$3 \times 3e_{1u}$	$5 \times 3e_{1u} +$ $4 \times 1b_{2u} +$ $4 \times 2b_{1u}$	$4 \times 3a_{1g}$	$8 \times 2e_{2g}$	$8 \times 2e_{1u}$
S_4 assignment	$2 \times (a+b+2 \times e)$	$b+2 \times e$	$2 \times (2 \times e+a)$ $+b$	$b+2 \times e$	$3 \times (a+b+2 \times e)$ $+a$	$a+b+2 \times e$	$2 \times (a+b+2 \times e)$	$2 \times (a+b+2 \times e)$
$C(C_6H_5)_4$	8.41, 8.97	10.93	11.68	13.22	13.82, 14.52	16.50	18.5	22.1
$Si(C_6H_5)_4$	8.96	10.17	11.63	12.89	13.72, 14.38	16.26	18.4	21.9
$Ge(C_6H_5)_4$	8.95	10.03	11.75	12.85	13.77, 14.26	16.17	18.4	22.4
$Sn(C_6H_5)_4$	9.04	9.77	11.55	12.74	13.99	16.01	18.5	21.9
$Pb(C_6H_5)_4$	8.95	8.37, 9.68 [b]	11.55	12.74	13.68, 14.14	16.2	18.4	22.0

[a] The e notation is used to represent a single orbital which will in the benzene situation be one of a degenerate pair but will not necessarily be so for the tetraphenyls.

[b] Structure probably due to large spin–orbit splitting associated with Pb 6p character. cf. $3t_2$ band of $Pb(CH_3)_4$ [8].

orbitals. This band moves to progressively lower ionization energies with the increasing atomic mass of the central atom reflecting the central atom character of the orbital. A similar trend was noted for the equivalent t_2 orbital in the $M(CH_3)_4$ spectra [8]. Band C then corresponds to ionization from the remaining 9 orbitals formed by weak interaction between the remaining five e_{2g} orbitals and the four a_{2u} orbitals. Band A is then assigned to 4 sets of weakly interacting $1e_{1g}\pi$ orbitals.

Although interaction between the metal $p't_2'$ orbital combination and the benzene $3e_{1u}$ and $3a_{1g}$ combinations is expected to be smaller than that with the $3e_{2g}$ combination, evidence of these interactions might be expected in the spectra. Thus band, D, which is simply a shoulder of band E in the $C(C_6H_5)_4$ spectrum, progressively separates from band E with increasing central atom mass. This, and its position with respect to the parent benzene band, associates band D with the t_2 $3e_{1u}$ orbital combination. A similar smaller shift associated with band F would appear to be associated with the M–X character of the $3a_{1g}$ combinations. Since this feature is well separated from adjacent bands it should be possible to observe the proposed 't_2', 'a_1' components. This has not, however, been observed, possibly due to the small splitting and the expected low intensity of the 'a_1' feature. In terms of the analysis given, band E then corresponds to ionization from the remaining 5 unperturbed $3e_{1u}$ orbitals and from orbitals derived from weakly interacting combinations of $1b_{2u}$ and $2b_{1u}$ orbitals (see Table 1).

So far only those orbital combinations involving central atom valence p character have been discussed. Both for MH_4 and for $M(CH_3)_4$ weak features on the high energy side of the spectrum have been associated with ionization from a_1 orbitals with substantial central atom valence s character. However, no such band has been observed for the Group IVB tetraphenyls. It seems likely that in this case the M valence s character is shared with the four possible a_1 C_{2s} type combinations, and that the resultant perturbation of the parent C_{2s} type orbital is too small to be observed. Bands corresponding to ionization from all 'C_{2s}' orbital combinations except to the innermost one are observed in the He(II) spectra (Fig. 2).

Additional support for the interpretation in terms of benzene parent orbitals comes from the fine structure observed for the various bands. It is notable that this is significantly greater for $C(C_6H_5)_4$ and $Si(C_6H_5)_4$ than for $Sn(C_6H_5)_4$ and $Pb(C_6H_5)_4$. This is in keeping with the expected increase in M–C bond lengths for the heavier metals, which will reduce the possibility of interaction between the phenyl ligands.

Extension of the energy range in the He(II) spectra reveals two further bands at 18 and 22 eV, which are formed from combinations of the benzene $2e_{2g}$ and $2e_{1u}$ carbon $2s$ orbital combinations, respectively. Ionization energies for all the bands discussed together with their assignments under S_4 symmetry are given in Table 1.

The He(I) photoelectron spectra of the triphenyl derivatives of Group IVB elements have also been reported [10]. Although slightly more complex than the spectra of the tetraphenyls, due to their lower symmetry, the spectra are broadly similar, displaying three main features at approximately 9, 12 and 14 eV ionization energy. These are equivalent to features A, C and E identified in the tetraphenyl spectra, and are presumably associated with orbitals of similar character. In particular, a band associated with the principal $M-C_3$ bonding orbital is identified in the 9 to 11 eV ionization energy region. This follows a similar trend to band B observed in this work and associated with the $M-C_4$ t_2 bonding orbital.

Calculations

The simple model used so far enables one to make reasonable deductions about orbital localization properties in relatively large molecules, but it is desirable to substantiate its predictions by quantum chemical calculations. The main aim of the calculations described below was not to obtain accurate MO energies, because no reliable assignment based on Koopmans' approximation can be expected for such large flexible molecules, but simply to gain some insight into the orbital localization properties and to deduce which orbitals have significant central atom character. The FORTICON 8 program package (QCPE 344) was used in the calculations because of its ability to deal with very large molecules. STO exponents of single ζ quality for Ge, Sn and Pb atomic valence orbitals were taken from ref. 11 while Coulomb integrals were approximated by valence state ionization energies deduced from Hinze and Jaffe's work [12] and Moore's tables [13]. Virtual d orbitals on the central atom were included in the basis set. The molecular geometry employed in the calculations was based on gas-phase electron diffraction data for tetraphenyltin [2]. Benzene rings were assumed to be regular hexagons and central atom valence angles to be equal to those in a regular tetrahedron (109.5°). The angle (φ) between the ring plane and the plane containing the M–C bond together with S_4 axis was fixed at 34.1° in all calculations except those for tetraphenylmethane, for which calculations were performed for two different geometries, φ 49° and φ 34.1°. The central atom valence bond lengths used in the calculations were taken from X-ray and electron diffraction data given in ref. 2, while the Pb–C bond length (2.19 Å) was that revealed by an X-ray diffraction study of tetraphenyllead [14].

Koopmans' theorem ionization energies obtained from these calculations cannot be regarded as a reliable guide to assignment, since even for the benzene spectrum in terms of which the tetraphenyl spectra have so far been discussed the calculation gives an ordering of ionized states differing markedly from the currently accepted assignment. However, although an incorrect ordering was predicted, many of the features deduced from the spectra were reproduced by the calculations. Thus the Koopmans' IE's for the tetraphenyls correlated well with those for benzene. The measurable interaction between the benzene orbitals in $C(C_6H_5)_4$ was indicated by a maximum spread in ionization energies calculated for this molecule. The $3e_{2g}$ orbitals were observed to split into a group of 3 with substantial central atom p character and a group of 5 largely unaffected orbitals. The central atom s character appeared to be shared between four of the C_{2v} combinations. These observations substantially support the major conclusions arrived at by interpreting the $M(C_6H_5)_4$ spectra in terms of four weakly interacting benzene rings.

Conclusions

It has been shown that the UV photoelectron spectra of the Group IVB tetraphenyl molecules can be interpreted in terms of a perturbed system of four weakly interacting benzene molecules. Assignments are made on this basis and conclusions concerning orbital character are shown to be in agreement with extended Hückel calculations on these systems. Trends in the ionization energy of the $M-(C_6H_5)_4$ bonding orbitals are similar to those observed for the equivalent orbitals in the case of $M(CH_3)_4$ [8] and $HM(C_6H_5)_3$ species.

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