X-RAY SPECTRAL STUDY OF THE ELECTRONIC STRUCTURE OF Ph_4Si and Ph_3SiH

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The structures of the molecular orbitals, including the 3p states of silicon, in Ph_4Si and Ph_3SiH have been studied from the Si K_β spectra. It has been established that the structure of the energy levels of these compounds consists of the system of molecular levels of benzene, weakly perturbed by interaction with the valence levels of silicon. It has been shown that the Si–Ph σ bonds are formed chiefly by molecular orbitals (MO) formed by the interaction of the 3p orbitals of silicon with the benzene orbitals $2e_{2g}$ and $2e_{1u}$. In Ph_4Si, the existence of very weak interactions of the $p_\pi-p_\pi$ type has been detected, and the intensity of these interactions increases considerably on going to Ph_3SiH.

The present paper describes a study of the structure of the molecular levels of tetraphenylsilane and triphenylsilane from the K_β x-ray fluorescence spectra of silicon. The Si K_β spectrum is produced as a result of electron transitions into the Si 1s level from levels whose MO contain an admixture of the 3p orbitals of silicon. According to the generally accepted interpretation of x-ray emission spectra, the integral intensities of the components of the spectrum are proportional to the squares of the coefficients of the corresponding atomic orbitals in the MO. The widths of the components are determined by the width of the internal level (0.44 eV), the distortion due to the apparatus (0.23 eV), and the extent of the multiplet and vibrational structures of the molecular levels. As a result, the components of the K_β spectrum are not always resolved sufficiently clearly, although they appear in the form of maxima and other characteristic features. The positions and integral intensities of the components have been found by breaking down the contour of the spectrum into dispersion components by the method of least squares.

It has been shown [1-3] that in the case of compounds of silicon with monatomic oxygen, nitrogen, and carbon ligands, the positions of the components of the Si K_β spectrum are determined by the 2p and 2s levels of the ligands. It may therefore be assumed that in the case of complex ligands also, the positions of the components of the Si K_β spectrum will be determined by their energy structure.

In the tetraphenylsilane molecule the silicon atom is surrounded by four benzene rings, in each of which it replaces one of the hydrogen atoms of the benzene. The replacement of hydrogen by silicon should not lead to appreciable perturbation of the molecular levels of benzene, since the electronegativities of hydrogen and silicon are close to one another. The main σ interaction of the 3p orbitals of silicon should take place with groups of benzene orbitals localized along the C–H bonds. These are the $2e_{2g}$, $2e_{1u}$, and $2a_{1g}$ orbitals, consisting chiefly of the $2p\sigma$ orbitals of carbon (to the extent of $\sim 70\%$) [4]. The $2e_{1u}$ and $2a_{1g}$ orbitals lie deeper, and will be perturbed to a lesser extent than the $2e_{2g}$ orbitals. The $2b_{1u}$ and $1e_{2g}$ orbitals, containing a considerable contribution from the 2s orbitals of carbon and the 1s orbital of hydrogen, also have favorable geometric conditions for the formation of σ bonds with the 3p orbitals of silicon. Thus the Si K_β spectrum of tetraphenylsilane should show at least five components.

The contour of the K_β spectrum of Ph_4Si, given in Fig. 1a, clearly shows components A, B, C, D, and E. In accordance with what has been said above, the less perturbed levels of benzene $2e_{1u}$ and $2a_{1g}$ must be associated with the components of the spectrum B and D. The other components can then be readily identified: The

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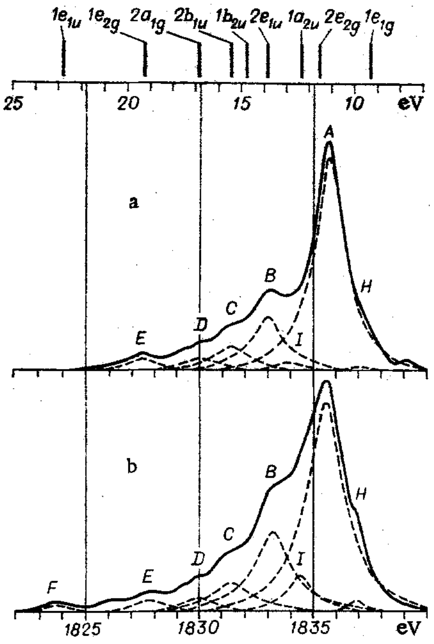

Fig. 1

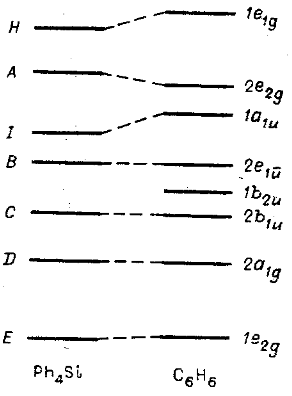

Fig. 2

Fig. 1. a) Si K_β spectrum of Ph_4Si and diagram of the ionization potentials of benzene [3]; b) Si K_β spectrum of Ph_3SiH.

Fig. 2. Diagram showing the correlation of the molecular levels of tetraphenylsilane and benzene.

maxima A, C, and E are produced as a result of electron transitions from molecular levels formed by the interaction of the 3p level of silicon with the $2e_{2g}$, $2b_{1u}$, and $1e_{2g}$ levels of benzene respectively (see Figs. 1 and 2). These components reflect the σ bonds between silicon and the phenyl rings.

The breakdown of the contour of the spectrum into dispersion components, in addition to those noted above, revealed two other components – I and H – with low intensity. These apparently originate in the interaction of the 3p orbitals of silicon with the ligand π orbitals $1a_{2u}$ and $1e_{1g}$.

From the ratio of the integral intensities of the components of the Si K_β spectrum (see Table 1), it follows that in Ph_4Si the Si–Ph bonds are predominantly σ bonds, and the $3p-2e_{2g}$ and $3p-2e_{1u}$ interactions are the strongest. Interactions of the π type with the $1a_{2u}$ and $1e_{1g}$ orbitals of benzene in tetraphenylsilane are revealed extremely weakly. There is no sign of interaction between the 3p orbitals of silicon and the $1b_{2u}$ orbital, which in benzene is responsible for the σ bonds in the ring and consists of the $2p_\sigma$ orbitals of carbon to the extent of 100% [4].

The contour of the Si K_β spectrum in triphenylsilane is given in Fig. 1b. It can be seen from Fig. 1 that the structure of the spectrum of this compound is also determined chiefly by the energy structure of benzene.

TABLE 1. Energy Positions E, Half-Widths γ, and Relative Integral Intensities I_i/I_A of the Components of the Si K_β Spectra

Component	Ph_4Si			Ph_3SiH		
	E, eV	γ, eV	$\frac{I_i}{I_A}$, %	E, eV	γ, eV	$\frac{I_i}{I_A}$, %
H	1837,00	1,20	2,0	1836,90	1,0	4,0
A	1835,65	1,6	100	1835,50	1,9	100
I	1833,90	1,3	2,4	1834,40	1,4	41,6
B	1833,00	1,8	27,0	1833,20	1,9	36,6
C	1831,40	1,8	12,0	1831,40	2,0	13,4
D	1830,00	1,6	5,5	1830,00	1,5	4,5
E	1827,50	1,4	4,3	1827,80	1,4	3,2
F	———	———	———	1823,80	0,8	1,0

In contrast to the previous case, however, the spectrum shows a long-wave component F and an increase in the relative intensity of the π components I and H. These changes in the spectrum reflect the following features: 1) On going from Ph_4Si to Ph_3SiH there is a decrease in the symmetry of the molecule from T_d to C_{3v}, leading to interaction between the Si 3p orbitals and the $1e_{1u}$ orbitals of benzene and the appearance of the F component. It may be noted that the orbital $1e_{1u}$ consists of the 2s orbitals of carbon to the extent of 73% [4]; 2) the decrease in symmetry is accompanied by an increase in the angles between the Si–C bonds, so that the molecule shows improved geometric conditions for π interaction with the phenyl rings. This leads to an increase in the intensity of the I and H components.

Silicon–hydrogen interaction is not revealed in the Si K_β spectrum of Ph_3SiH. The 1s orbitals of hydrogen apparently make contributions to the σ MO of triphenylsilane.

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THE PHOTOEFFECT YIELD SPECTRA OF BERYLLIUM COMPOUNDS

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The photoeffect yield spectra (PYS) from the Be1s level of various Be compounds in the energy range 100-250 eV have been studied experimentally. The position of the Be K absorption edge was determined from the position of the center of the rising section of the first maximum in the PYS. A systematic increase in the energy of the Be K absorption edge was observed in the series $BeO-BeSO_4 \cdot 4H_2O-Be(OH)_2-Be(COOCH_3)_2-BeF_2$ as the oxygen atoms in the first coordination sphere of the Be atom are replaced by water molecules, hydroxyl groups, acetate groups, and fluorine atoms by 0.4, 0.6, 1.1, and 2.0 eV, respectively, relative to BeO. It has been shown that changes in the ligands in the second and subsequent coordination spheres influence the position of the Be K absorption edge.

The present paper describes a study of the influence of the environment of the beryllium atom on the energy positions of the details of the photoeffect yield spectra from the Be1s level of various compounds. This work is a continuation of studies of the energy structure of inorganic and organic compounds of beryllium [1, 2].

The photoeffect yield spectra were obtained on an RSM-500 spectrometer–monochromator [3] with an energy resolution of 0.3 eV. The x-ray tube operated at 5 kV and 100-200 mA, and a tungsten plate was used as the anode. The substance being studied was deposited on aluminum foil by means of an adhesive or by depositing a suspension of the substance in acetone. Nickel foil and gold foil were used as photocathodes with known efficiency. The spectra were recorded by measuring points and by means of a recorder. The displacement of the maxima was determined relative to the line $WN_V-N_{VI,VII}$ (212.2 eV).

The state of the surface of the photocathode is of decisive importance in photoeffect yield spectroscopy, since the depth of the yield of the electrons produced on the absorption of x radiation is small. For hygro-

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