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Investigating the Electronic Structure of Tetramethylsilane by Means of X-Ray Spectroscopy and Theoretical Calculations

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Abstract—The electronic structure of a tetramethylsilane molecule $Si(CH_3)_4$ is studied via X-ray fluorescence spectroscopy and simulations based on the density functional theory. An analysis of the molecular orbitals is conducted on the basis of the calculations, and a theoretical SiK_{β_1} X-ray fluorescence spectrum is constructed that appears to be in good agreement with the experimental findings. The main types of chemical interactions between the silicon atoms and carbon atoms of methyl groups are revealed.

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INTRODUCTION

Investigations of the electronic structure of silicon compounds via X-ray fluorescence spectroscopy began in the 1960s and 1970s. The first objects of research were mainly such simple inorganic compounds as Si, SiO_2, SiH_4, Si_3N_4, and SiC [1]. The electronic structure of diverse siliconorganic compounds was later studied by means of X-ray spectral analysis [2–9]. In [8], the SiK_β X-ray fluorescence spectrum of tetramethylsilane was constructed and analyzed using the results from quantum-chemical calculations and the semiempirical CNDO/2 method. Despite the data acquired with CNDO/2 being semiquantitative, the authors obtained information on a complete set and symmetry of levels and the approximate sequence and population of its atomic orbitals (AOs), and compared them to X-ray spectral analysis data. The comparison of the calculated and experimental results in [8] revealed that the CNDO/2 semiempirical method correctly conveyed the sequence of tetramethylsilane levels; however, the absolute values of energy parameters ε_i were close (±1 eV) to the respective ionization potentials (IPs) only after reducing them by a factor of 1.5 (done by intentionally selecting the CNDO/2 parameters). The authors of [8] thereby inferred that the results from quantum-chemical calculations using the CNDO/2 method for siliconorganic molecules did not allow them to obtain sufficiently reliable data.

More reliable theoretical data for $Si(CH_3)_4$ were acquired in [10, 11], where photoelectron spectra (PESes) were treated using calculations for the molecular orbitals (MOs) of this compound in the MS-X_α approximation. Conclusions regarding the composition of the valence band levels were drawn, based on the calculations and an analysis of changes in the intensity of photoelectron lines with varying exciting energy. The theoretical IPs of levels obtained using Koopmans' theorem diverged from the experimental data by 1 to 3 eV, indicating the importance of allowing for electron correlation.

In this work, the density functional theory (DFT) was used to interpret the SiK_{β_1} X-ray fluorescence spectrum of $Si(CH_3)_4$. It had already proven to be highly accurate in calculating the ionization energies of MOs of siliconorganic complexes, so much so that it was comparable to the accuracy of X-ray spectral experiments [12–14]. Interest in investigating the electronic structure of tetramethylsilane $Si(CH_3)_4$ was stimulated by its wide application in organic and organoelement synthesis, e.g., in obtaining hollow-fiber gas-separation membranes with high degrees of separation of oxygen and nitrogen, or as a stereospecific polymerization catalyst. Utilizing current methods for calculating electronic structure in combination with the results from X-ray spectral experiments allows us to obtain comprehensive information on chemical interactions in a studied compound and ensures prediction of its characteristics of practical importance.

EXPERIMENTAL

The SiK_{β_1} X-ray fluorescence spectrum of $Si(CH_3)_4$was recorded on a DRS-2M Johann-type focusing spectrograph [15]. A quartz crystal analyzer ($10\bar{1}0$) with a 500 mm radius of curvature was used. The resolution of the spectrograph measured with the Co$K_{\alpha_{1,2}}$ doublet was 15000, which corresponds to instrumental distortion in the 0.15 eV region of the analyzed line.

THEORETICAL CALCULATIONS

The atomic and electronic structure of the $Si(CH_3)_4$ molecule were calculated by means of density functional theory (DFT) using the Gaussian-03 software package [16]. The geometry and obtaining partial electronic states distribution (PESD) of a molecule were optimized using a B3LYP hybrid functional with its correlation part in the Lee–Yang–Parr form [17] and its exchange part in the Becke form [18]. The initial atomic coordinates needed for optimization were taken from the crystallographic data for the $Si(CH_3)_4$ compound [19, 20]. The standard extended split-valence basis set 6-311G** was chosen for our calculations.

The X-ray transition energies $E_{i,j}$ were calculated as the differences between the energies of valence ε_i and inner ε_j levels found in the frozen orbital approximation (i.e., vertical IPs found using Koopmans' theorem, Eq. (1)):

$$E_{i,j} = \varepsilon_i - \varepsilon_j. \quad (1)$$

To obtain the SiK_{β_1} X-ray emission spectrum, the calculated C_{ij} ($j = 3p$) coefficients were summed using Eq. (2) for silicon atoms [21]:

$$I_{ij}^A \sim N\Sigma_i \left|C_{ij}^A\right|^2, \quad (2)$$

where C_{ij}^A are the LCAO coefficients with which i and j AOs are included in the selected MOs, and N is the normalization factor. In constructing the X-ray emission spectrum, the discrete lines that arose due to transitions from certain MOs were broadened using a Lorentz function with width parameter $\gamma = 0.5$ eV.

RESULTS AND DISCUSSION

The SiK_{β_1} X-ray fluorescence spectrum of $Si(CH_3)_4$is generated by electronic transitions from molecular levels to previously ionized Si 1s silicon level according to dipole selection rules. Only those electron energy levels that correspond to MOs containing Si 3p AO are reflected in the SiK_{β_1} X-ray spectra, with the integral intensity of the spectral components being proportional to the Si 3$p$occupation of the respective MOs. The opportunity to gain information on the symmetry and AO occupation of MOs is a unique trait of the X-ray spectral technique.

Figure 1 shows the PES for $Si(CH_3)_4$ [10], the diagram of electron energy states for $Si(CH_3)_4$, and (a) the form of the isosurfaces of selected MOs, (b) the experimental SiK_{β_1} spectrum and PESD of Si (s, p, d), and (b, c) the PESDs of C (s, p) and H (s). A comparison of the fine structure of the experimental SiK_{β_1} spectrum, composed of components A, B, and C, and the theoretical PESD of Si (p), which is in fact the theoretical SiK_{β_1} spectrum, demonstrates that our calculations conveyed the shape and energy structure of the

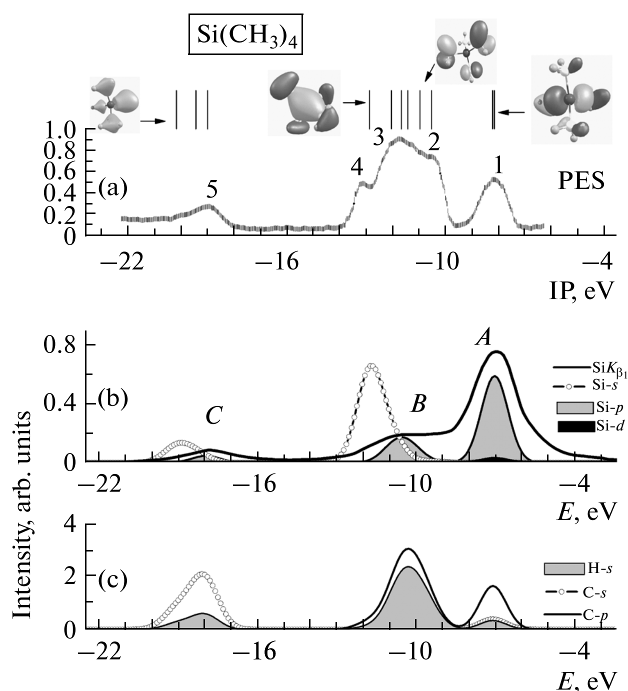

Fig. 1. (a) Photoelectron spectrum [10], energy structure of tetramethylsilane MOs, and the isosurfaces of some MOs; (b) the SiK_{β_1} X-ray fluorescence spectrum of $Si(CH_3)_4$; and (b, c) the PESDs of Si(s, p, d), C(s, p), and H(s).

SiK_{β_1} X-ray emission spectrum very well. The SiK_{β_1} X-ray emission spectrum was matched with the theoretical one by allowing for the minimal shift in the energy position of components from the PESD maxima of Si 3p. The PI value in the PESes of $Si(CH_3)_4$ differed from the same values obtained using Eq. (1) by approximately 1 eV. Such reduced PI values derived using Koopmans' theorem are typical for the calculations performed via DFT using the B3LYP functional [22]. The PES scale in Fig. 1 is shifted by 1 eV relative to the energy scale of the calculations. Joint analysis of the experimental and theoretical data gives a full picture of the participation of all AOs in the formation of MOs of $Si(CH_3)_4$.

The table gives the ε_i energies, the composition of MOs, and the respective main types of chemical bonds in $Si(CH_3)_4$.

From a comparison of the PES [10] and SiK_{β_1} X-ray emission spectrum of $Si(CH_3)_4$, we can see that the energy positions of the components of these spectra coincide with an accuracy of 0.1–0.2 eV (with allowance for the shift). Spectral band 1 in the PES corresponds to short-wave component A in the SiK_{β_1} spectrum, which is associated with chemical bonding between Si 3p AO of silicon and C 2p AO of carbon of methyl groups [10, 11]. According to our calculations (table), these spectral maxima are due to the elec-

Components of the SiK_{β_1}- X-ray emission spectrum, energies ε_i and composition of MOs, and chemical bond types for $Si(CH_3)_4$

SiK_{β_1}-components	ε MO, eV	Si, %	C, %	H, %	Chemical bond types
	−7.09	20(*p*)+1(*d*)	13(*s*)+56(*p*)	11(*s*)	
A	−7.09	20(*p*)+1(*d*)	11(*s*)+55(*p*)	14(*s*)	σ(*p*,*d*Si-*s*,*p*C)
	−7.15	19(*p*)+1(*d*)	15(*s*)+56(*p*)	10(*s*)	
	−9.46	1(*s*)	54(*p*)	45(*s*)	
	−9.89	1(∂)	55(*p*)	44(*s*)	σ(*p*C-*s*H)
	−9.89	1(∂)	55(*p*)	44(*s*)	
B	−10.35	3(*p*)	54(*p*)	43(*s*)	
	−10.35	3(*p*)	54(*p*)	43(*s*)	σ(*p*Si-*s*,*p*C-*s*H)
	−10.60	3(*p*)	2(*s*)+51(*p*)	44(*s*)	
	−10.60	3(*p*)	2(*s*)+51(*p*)	44(*s*)	
	−10.97	14(*s*)+7(*p*)	34(*p*)	45(*s*)	σ(*s*,*p*Si-*p*C-*s*H)
	−11.81	62(*s*)	19(*p*)	19(*s*)	σ(*s*Si-*p*C-*s*H)
	−17.91	2(*p*)	74(*s*)+1(*p*)	21(*s*)	σ(*p*Si-*s*,*p*C-*s*H)
C	−17.91	2(*p*)	74(*s*)+1(*p*)	21(*s*)	
	−18.36	6(*s*)+1(∂)	63(*s*)+1(*p*)	29(*s*)	σ(*s*,*p*Si-*s*,*p*C-*s*H)
	−19.09	11(*s*)	67(*s*)+1(*p*)	21(*s*)	(*s*Si-*s*,*p*C-*s*H)

tronic transitions from three practically degenerate MOs with the energies in the region of −7.0 to −7.15 eV. The greatest contribution to these MOs is that of Si *p*-orbitals. It is noteworthy that the Si *d*-orbitals of silicon also contribute weakly to the formation of these MOs.

The wide band in the PES (bands 2 and 3) corresponds to component *B* in the SiK_{β_1} spectrum. These PES maxima are attributed principally to σ-interaction between the carbon and hydrogen atoms of methyl ligands. The appearance of low-intensity maximum *B* in the SiK_{β_1} spectrum indicates negligible admixing of the Si 3*p* AO of silicon to these MOs, which is also apparent from the form of the MO isosurfaces. The table also shows that the Si 3*p* occupation values for MOs in the region of −9.46 to −10.97 eV are several times lower than those for the higher MOs. Maximum 4 in the PES corresponds to a separate MO with an energy of −11.81 eV composed of mainly Si 3*s* AO of silicon; however, this MO is not reflected in the SiK_{β_1} spectrum, due to the selection rules.

Component *C* in the SiK_{β_1} spectrum and band 5 in the PES reflect σ bonding between the silicon atom and the carbon atoms with a dominant contribution from the C *s*-states and slight admixing of the Si *p*-states. These deeply-lying MOs (−17.91 to −19.09 eV) are localized mainly on methyl ligands.

As was demonstrated above, the integral intensities of the SiK_{β_1} X-ray emission spectrum are proportional to the contributions from the Si 3*p* AO of silicon. The normalized ratios of integral intensities $I_A : I_B : I_C$ obtained from the SiK_{β_1} spectrum of $Si(CH_3)_4$were 1.0 : 0.24 : 0.10, which corresponded well to the calculated ratios of 3*p* occupations of silicon in MOs of 1.0 : 0.23 : 0.05.

CONCLUSIONS

The sequence and characteristics of MOs of tetramethylsilane were determined from an analysis of the SiK_{β_1} X-ray emission spectrum and quantum-chemical calculations. The experimental X-ray spectral data agreed well with the theoretical calculations made in approximation of the density functional theory.

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