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COMPARATIVE STUDY OF Si-2*p* CORE-EXCITATION SPECTRA OF SiX₄ MOLECULES (WITH X = H, D, F, Cl, Br)

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Highly-resolved photoabsorption spectra of SiX₄ molecules (with X = H, D, F, Cl, Br), recorded by photoionization in the region of the Si-2*p* absorption thresholds, are presented. Vibrational fine structure could be resolved in all cases, allowing a derivation of vibrational energies and intra-molecular distances of the core-excited molecules from Franck-Condon fits. In case of the heavier ligand atoms, spectral features arising from thermally-excited vibrational states of the electronic ground state were observed. The results obtained for the various ligand atoms are compared with each other and are discussed in the context of the equivalent-cores approximation.

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Recent improvements in high-resolution soft X-ray monochromators at synchrotron-radiation storage rings have allowed the acquisition of a number of vibrationally-resolved photoabsorption spectra of core-excited molecules. Such core-excitation spectra with vibrational splittings are usually due to excitations from the lowest vibrational substate of the electronic ground state, $v'' = 0$, to vibrational substates of core-excited states of a molecule, v' . In this paper we report on a study of vibrational splittings in Si-2*p* core-excited SiX₄ molecules, with X = H, D, F, Cl, and Br. For the lightest molecule, silane (SiH₄), vibrational substates have been first resolved by Hayes et al. [1], while for SiX₄ molecules with the heavier ligands F and Cl vibrational fine structure could be resolved only recently [2, 3], since the vibrational energies decrease with increasing mass of the ligand atoms. In the present work, vibrational splitting in core-excitation spectra was first resolved for SiBr₄, and the results will be compared with the analogous fine structures of the other SiX₄ molecules. All of the measured spectra were analyzed on the basis of the Franck-Condon principle, i.e. vibrational energies in the excited states and changes of intra-molecular distances, ΔR , between the ground states and the core-excited states were derived from the intensity distribution in the vibrationally-resolved spectra [4].

Many of the spectroscopic details of core-excited molecules can be understood on the basis of the $Z + 1$ approximation, where equivalent cores are assumed

for a core-excited molecule containing atom Z and a valence-excited molecule containing atom $Z + 1$. This leads to similar valence-electronic states in the two cases, and allows e.g. to compare core-excited SiH_4 with valence-excited PH_4 or PH_4^+ . Molecular geometries and vibrational energies are expected to depend on the valence-electron configuration, allowing an estimate of the properties of Rydberg states of a core-excited molecule from those of valence-ionized states of the $Z + 1$ molecule.

The experiments were performed with the plane-grating SX700/II monochromator operated by the Freie Universität Berlin at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY). In the Si-2*p* excitation region ($h\nu \approx 110$ eV), an instrumental resolution of ≤ 15 meV (FWHM) can be obtained [5]. The photoabsorption spectra were recorded with a gas ionization cell separated from the ultra-high vacuum of the monochromator by a 1200 Å thick carbon window. Using a pressure of typically 0.1 mbar, the total photoionization current was monitored as a function of photon energy.

In general, photoabsorption spectra of core-excited molecules contain spectral features from excitations to valence and to Rydberg states, which can be distinguished by their widths, i.e. broad features from valence excitations and narrow resonances from Rydberg excitations [2, 3]. In the present work, only Rydberg excitations will be discussed. In Fig. 1, the Rydberg region of SiF_4 is shown, since it is representative for all SiX_4 molecules studied. The spectral features in Fig. 1 result from $v'' = 0 \rightarrow v' = 0$ Rydberg excitations plus additional excitations to higher vibrational states ($v'' = 0 \rightarrow v' = 1, 2, 3 \dots$). The structure of the spectrum arises from two *ns*, *np*, and *nd* series each, which converge towards the two spin-orbit split ionization thresholds $2p_{3/2}^{-1}$ (L_{III}) and $2p_{1/2}^{-1}$ (L_{II}). In the energy region above 110.2 eV, the vibrational fine structures of the Rydberg states ex-

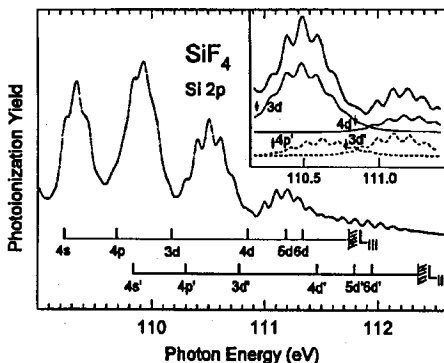


Fig. 1. Rydberg region of the Si-2*p* photoabsorption spectrum of SiF_4 . The observed resonances $2p_{3/2}^{-1}nl$ ($2p_{1/2}^{-1}nl$) are marked by $nl(nl')$; the vertical bar diagrams mark the $v'' = 0 \rightarrow v' = 0$ excitations. Insert: detail of the spectral region dominated by the $2p_{3/2}^{-1}3d$ and $2p_{1/2}^{-1}4d$ excitations, with results of the Franck-Condon analysis; the $v'' = 0 \rightarrow v' = 0$ transitions are marked by vertical arrows. The solid (dashed) subspectra represent excitations from the Si $2p_{3/2}$ (Si $2p_{1/2}$) core level.

hibit single vibrational modes, which — on the basis of their vibrational energies — can be assigned to the symmetric-stretching modes. As is obvious from the intensity distributions of the vibrational substates, not the $v'' = 0 \rightarrow v' = 0$ Rydberg excitations (indicated by bars) are the most intense ones, but excitations to higher substates (with $v' = 3$). This can be quantitatively described on the basis of a Franck-Condon analysis, where a strong change in the intra-molecular equilibrium distances between ground and excited state causes the observed intensity distribution. For the lowest Rydberg states, $4s$ and $4s'$, additional bending-mode vibrational states are excited (see below).

Figure 2 displays particularly interesting sections of the Si- $2p \rightarrow$ Rydberg excitation spectra of (a) SiCl_4 and (b) SiBr_4 , namely the $2p_{3/2}^{-1}4s$ Rydberg resonance with its vibrational substates, including the results of a Franck-Condon analysis. The observed vibrational splitting shows that the fine structure is due to the symmetric-stretching vibrational mode, with an intensity distribution of the vibrational substates similar to the one observed for SiF_4 . In addition to

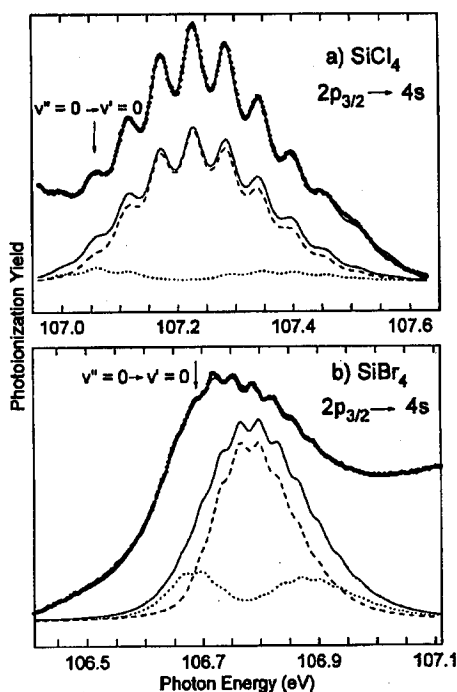


Fig. 2. Results of a Franck-Condon analysis of the $2p_{3/2}^{-1}4s$ resonances of (a) SiCl_4 and (b) SiBr_4 , with the $v'' = 0 \rightarrow v' = 0$ transitions marked by vertical arrows. The solid subspectra consider excitations from thermally excited vibrational sublevels in the electronic ground state, while the dashed subspectra neglect such "hot bands" (i.e. only $v'' = 0 \rightarrow v' = 0, 1, 2 \dots$ excitations are considered). The dotted subspectra represent the pure contributions from the "hot bands" ($v'' = 1, 2 \dots \rightarrow v' = 0, 1, 2 \dots$ excitations).

$v'' = 0 \rightarrow v' = 0, 1, 2, 3 \dots$ excitations (dashed subspectra), we observe also spectral features (dotted subspectra) which originate from thermally excited vibrational substates of the electronic ground state, $v'' = 1, 2 \dots$ ("hot bands"). The contribution from hot bands is larger for SiBr_4 than for SiCl_4 due to the increasing thermal population of ground-state vibrational states with decreasing vibrational energy, i.e. heavier ligand atoms. Hot-band contributions to core-level photoabsorption spectra have been first observed only recently [2], since a noticeable occupancy of ground-state vibrational states requires vibrational energies ≤ 50 meV and hence high spectral resolution.

TABLE

Vibrational energies, $\hbar\omega''$ and $\hbar\omega'$, and intra-molecular equilibrium distances, R_g and R_e , in the ground and excited states, respectively. The numbers for the core-excited molecules were obtained in the present work from Franck-Condon analyses. For comparison, the vibrational energies and equilibrium distances of the ionized $Z + 1$ molecules, PX_4^+ , are given in the last two columns. The numbers in parentheses represent the error bars in units of the last digit.

	$\hbar\omega''$ [meV]	$\hbar\omega'^a$ [meV]	R_g [Å]	R_e^a [Å]	$\hbar\omega$ [PX_4^+] [meV]	R [PX_4^+] [meV]
SiH_4	271.13 ^b	298.5(1.0)	1.471 ^c	1.417(2)	284.5 ^d	1.42(2) ^e
SiD_4	193.8 ^b	212.9(1.0)	1.471 ^c	1.417(2)	205.1 ^d	1.42(2) ^e
SiF_4	99.18 ^f	109.0(2.0)	1.554 ^g	1.486(2)	—	—
SiCl_4	52.69 ^h	58.1(0.5)	2.019 ⁱ	1.953(3)	55.8 ^j	1.97(1) ^k
SiBr_4	30.87 ^h	33.0(2.0)	2.150 ^l	2.103(2)	28.1 ^j	—

^athis work; ^bRef. [8]; ^cRef. [9]; ^dRef. [10]; ^eRef. [11]; ^fRef. [12]; ^gRef. [13]; ^hRef. [14]; ⁱRef. [15]; ^jRef. [16]; ^kRef. [17]; ^lRef. [18].

Table summarizes the results of the Franck-Condon analysis for the SiX_4 molecules. It includes the results for the symmetric-stretching vibrational energies, $\hbar\omega'$, and the intra-molecular equilibrium distances, R_e , in the core-excited states. In all cases, the symmetric-stretching vibrational energies in the excited state are $\approx 10\%$ larger than in the ground state, and the equilibrium distances decrease upon excitation by ≈ 0.06 Å. The observed variation of the intensity distributions of the vibrational substates are due to the different ligand-atom masses and not caused by different changes of the intra-molecular distances upon core excitation. Both effects are caused by a contraction of the valence orbitals due to the effective charge of the Si-2*p* core hole. The vibrational energies and equilibrium distances of the core-excited molecules are in close agreement with the values listed in the last two columns for the valence-ionized $Z + 1$ molecules, supporting the concept of the equivalent-cores approximation.

Figure 3 shows the spectral regions around the lowest Rydberg states in the Si-2*p* core-excitation spectra of SiH_4 and SiD_4 ; here, the $v'' = 0 \rightarrow v' = 0$ excitations and those to symmetric-stretching-mode vibrational substates are in-

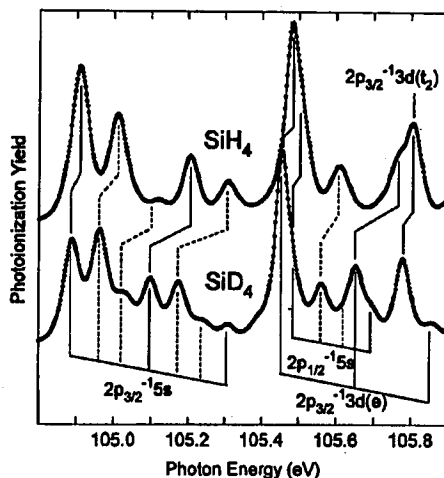


Fig. 3. Spectral regions around the lowest Rydberg states in the SiH_4 (upper) and SiD_4 (lower) core-excitation spectra, including the $2p_{3/2}^{-1}5s$, $2p_{1/2}^{-1}5s$, $2p_{3/2}^{-1}3d(e)$, and $2p_{3/2}^{-1}3d(t_2)$ resonances. Note that the energies of the $v'' = 0 \rightarrow v' = 0$ excitations of SiH_4 and SiD_4 differ by 25 meV due to an isotopic effect on the zero-point vibrational energies [6]. The $v'' = 0 \rightarrow v' = 0$ transitions and the excitations to symmetric-stretching-mode vibrational states are designated by solid vertical bars. Bending-mode vibrational states are identified by dashed vertical bars; these latter vibrations are clearly absent in case of the $2p_{3/2}^{-1}3d$ resonances.

indicated by solid vertical bars. In case of the lowest Rydberg states, $2p^{-1}5s$, additional vibrational modes are excited, which are designated by dashed vertical bars. These excitations are assigned to bending-mode vibrational substates on the basis of their low vibrational energies [7]. For higher Rydberg states, as the $2p_{3/2}^{-1}3d(e)$ resonance, these bending-mode vibrations are not observed, similar to the case of SiF_4 . The excitation of bending-mode vibrations can be explained by a lowering of the symmetry of the core-excited state as compared to the tetrahedral symmetry of the ground state of SiX_4 . The $2p^{-1}5s$ state is assumed to be a mixed state, i.e. a Rydberg state with some contributions from excitations to valence orbitals. This mixed state leads to a negative partial charge in the valence orbital region which interacts with the bonding electrons leading to a deformation of the molecule [7].

In summary, we have resolved vibrational fine structure in the Si-2p core-excitation spectra of SiX_4 molecules using high-resolution photoabsorption spectroscopy. A symmetric-stretching vibrational splitting was observed for all Rydberg states. For the lowest Rydberg states in SiH_4 , SiD_4 , and SiF_4 , splittings due to bending-mode vibrations were observed, which arise from the mixed-state character of these resonances. Franck-Condon analyses of the vibrationally-resolved spectral shapes were performed, and the derived results for vibrational energies and intra-molecular distances were found to be in good agreement with expectations from the $Z + 1$ approximation.

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