

Vibrationally resolved Si 2p photoabsorption spectrum of SiCl₄

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We report on a high-resolution study of the Si 2p photoabsorption spectrum of SiCl₄ in the gas phase. Characteristic differences in the intrinsic widths of the resonance lines allow a distinction of excitations to valence and Rydberg orbitals, respectively. The Rydberg resonances are found to be narrow and split into vibrational substrates from symmetric-stretching vibrations, providing information—on the basis of a Franck-Condon analysis—on vibrational energies and equilibrium internuclear distances of the core-excited molecule. Thermal population of excited vibrational levels in the molecular ground state has to be taken into account for a proper description of the spectrum.

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I. INTRODUCTION

Due to considerable progress in the monochromatization of soft x rays, high-resolution studies of inner-shell excitation spectra of a number of small molecules were recently performed. Some of these studies succeeded in resolving vibrational splittings of the core-excited states. These measurements were predominantly performed on the 1s levels of C, N, and O in, e.g., N₂ [1], CO [2], H₂CO [3], C₂H₄ [4], and CH₄ [5], which exhibit well-separated Rydberg states that converge to single ionization thresholds, with vibrational energies of the order of $\cong 200$ meV. A full understanding of such core-excitation spectra is particularly difficult if the various Rydberg series overlap and converge to *different* thresholds, as is the case, e.g., in 2p core excitation. Then, additional complications can arise from overlapping $2p^{-1}ns$ and $2p^{-1}nd$ (and occasionally also $2p^{-1}np$) Rydberg series. Fortunately, vibrational excitations are weak in most cases or can even be neglected, which means that they do not significantly influence the assignment of Rydberg states. Such situations have been found with the S 2p excitation spectra of SF₆ [6] and H₂S [7] as well as the Cl 2p spectra of HCl and Cl₂ [8]. One notable exception is known in the form of the Si 2p excitation spectrum of SiH₄, with strongly overlapping Rydberg series and vibrational sidebands [9]. Moreover, “forbidden” asymmetric vibrations were found to be excited in SiH₄, similarly to CH₄, which were interpreted on the basis of deviations from T_d symmetry in the tetrahedral molecule.

For other SiX₄ molecules with heavier ligand atoms X, vibrational splittings in the photoabsorption spectra are expected to be much smaller than in SiH₄; accordingly, they have not been resolved up to now, due to lack of resolution. On the other hand, strong vibrations must also be expected for these molecules, which supposedly are the reason for the observed discrepancies between calculated and measured linewidths in all cases except SiH₄ [10]. Moreover, the internuclear equilibrium distances of the (Z + 1) molecules PX₄ and PX₃, which—on the basis of the equivalent-cores (Z + 1) model—correspond to

those of the core-excited molecules SiX₄ and SiX₃, respectively, differ appreciably from the ground-state values of the SiX₄ molecules. This should give rise to strong excitations to high vibrational levels. Similarly, photoemission spectra observed for various silicon compounds could be fitted well by assuming vibrational energies equal to those of the corresponding (Z + 1) molecules PX₄ and PX₃ [12], although vibrational splittings could not be resolved, except in the case of SiH₄ and partly also in the case of SiF₄ [11].

For SiCl₄, a photoabsorption study performed with a resolution of $\cong 100$ meV has been reported, and the observed spectral features were assigned to spin-orbit-split excitations [13]. The measured spectrum was found to consist of excitations to localized valence orbitals and to Rydberg orbitals. The two types of excitations could be distinguished by a comparison of gas-phase and condensed-phase spectra [14], assuming that condensation influences only Rydberg orbitals. Various calculations of molecular orbitals in SiCl₄ have been performed [15–17], but the results could not explain up to now the measured spectral features in a satisfactory way.

In the present work, we report on a high-resolution [$\Delta E \cong 10$ meV, full width at half maximum (FWHM)] photoabsorption study of SiCl₄ in the gas phase. We find that due to the high spectral resolution valence and Rydberg orbitals can be readily distinguished on the basis of the intrinsic widths of the resonance lines. The Rydberg transitions exhibit extensive Si-Cl vibrational structures, which are analyzed on the basis of the Franck-Condon model. As a result, the vibrational frequencies, the anharmonicities, and the internuclear equilibrium distances were derived for the core-excited molecule.

II. EXPERIMENT

The measurements were performed with the high-resolution plane-grating SX700/II monochromator [18], operated by the Freie Universität Berlin at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY). The spectra were taken with a 2442 lines/mm

grating, with the electron-storage ring operated in the small-source mode (vertical source size was ≈ 0.15 mm); this results in an overall resolution of ≈ 10 meV (FWHM) at $h\nu \approx 108$ eV. The photon energy was calibrated by monitoring the $N\ 1s \rightarrow \pi^*$ ($v''=0 \rightarrow v'=0$) excitation in N_2 at 400.88 eV and the He ($sp, 23-$) double-excitation resonance at 62.758 eV [19]. The photoabsorption spectra were recorded by monitoring the total photoionization yield as a function of photon energy using an ionization cell of 10 cm active length [18]; it was separated from the ultrahigh vacuum of the monochromator by a 1200-Å-thick carbon window, and filled with typically 0.1 mbar of $SiCl_4$ gas. For such low pressures saturation effects are negligible, and the total photoionization yield is proportional to the photoabsorption cross section. Vapor-phase $SiCl_4$ was introduced by pumping liquid-phase silicon chloride; its cleanness was checked by the absence of N 1s and O 1s excitations in the photoabsorption spectra.

III. EXPERIMENTAL RESULTS

In Fig. 1, an overview of the Si $2p$ photoabsorption spectrum of $SiCl_4$ is presented. The coarse spectral features are characterized by spin-orbit-split resonances, which are designated according to Ref. [13] as 1 ($1'$), . . . , 6 ($6'$) for $2p_{3/2}^{-1}$ ($2p_{1/2}^{-1}$) excitations at photon energies of 104.34 eV (104.94 eV), . . . , 109.96 eV (110.52 eV). In the spectrum shown, at least six spin-orbit-split resonances can be identified, and there is an additional fine-structure splitting of all features above 107 eV. This fine-structure splitting with a peak-to-peak separation of ≈ 58 meV can be easily ascribed to a vibrational splitting from symmetric Si-Cl vibrations, since the energy splitting is close to that of the symmetric-stretching vibrational mode in the ($Z+1$) molecule PCl_3 , with a vibrational

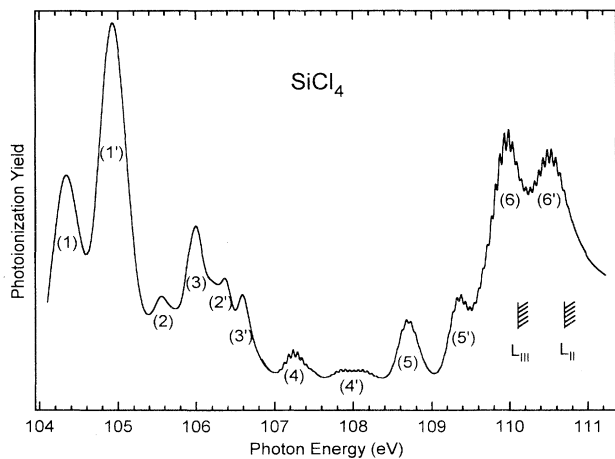


FIG. 1. Overview of the Si $2p$ core-excitation spectrum of $SiCl_4$ in the gas phase. The total photoionization yield, which is proportional to the photoabsorption cross section, is plotted as a function of photon energy. The L_{II} and L_{III} ionization thresholds are marked by solid vertical bars. All resonances are found to be spin-orbit split (primed and unprimed numbers).

energy of 65 meV [12]. In the case of resonances below 107 eV (resonances number 1, 2, and 3), the intrinsic widths are obviously too large to allow such vibrational fine structures to be resolved; these resonances have predominantly valence character. Vibrational fine structure is only observed for the long-lived states with energies above 107 eV, which we consequently assign to rather pure Rydberg states. This conclusion is in agreement with the results of a recent study of $SiCl_4$ in the condensed phase, where only excitations into orbitals with strong valence character survived condensation, while all Rydberg states at energies between 107 and 109.5 eV were found to be quenched [14]. We argue that in high-resolution studies the intrinsic linewidth can be used as a suitable parameter to distinguish between (broad) valence states and (narrow) Rydberg states. It is interesting to note that there seems to be a relatively abrupt change from valence to Rydberg excitations between peak 3 and peak 4, with the latter exhibiting already a narrow linewidth and hence a resolved vibrational fine structure. At higher energies (peaks number 6 and $6'$), there is an overlap of Rydberg states with valence states both at ≈ 109.96 and at ≈ 110.52 eV, leading to vibrationally split resonances, which are on two relatively broad structures; the latter were visible in the condensed-phase spectra as well [14]. It is possible that similar overlap of valence and Rydberg states occurs at $h\nu \approx 107.4$ eV, since a weak spectral feature has also been found at this energy in the condensed-phase spectrum [14].

The spectra were analyzed by assuming a constant spin-orbit splitting of ≈ 610 meV. Both the valence and the Rydberg states exhibit more transitions than have been reported in the literature [13]. In the valence-state region, at least four spin-orbit-split transitions can be assigned, which show additional overlap with the first Rydberg excitation (peak 4). According to theoretical work [15–17], the lowest spin-orbit-split valence state at 104.34 and 104.94 eV (peaks 1 and $1'$) has a_1 symmetry, but the assignment of the higher resonances is still controversial. Although we were also not able to assign the higher valence states unambiguously, we think that we can give a clear peak characterization in the Rydberg-state region from the derived quantum defects, assuming energies of 110.099 ± 0.020 and 110.698 ± 0.020 eV, respectively, for the $2p_{3/2}(L_{III})$ and $2p_{1/2}(L_{II})$ thresholds. These threshold energies were obtained from the positions of the nd states (see below) and by applying the Rydberg formula; they differ by ≈ 70 meV from those reported in Ref. [13]. In the present characterization, we obtain quantum defects of ≈ 2.0 , ≈ 1.4 , and ≈ 0.1 for the s , p , and d states, respectively. A different assignment of the Rydberg states, however, would not change the Franck-Condon analysis given further below. Note that quantum defects are sometimes given in the literature with 1 added to the values we are quoting here (see, e.g., Ref. [9] for SiH_4).

The lowest Rydberg resonance (peak 4) is accordingly assigned to a $Si\ 2p_{3/2} \rightarrow 4s$ transition with vibrational splitting. The next-higher Rydberg resonance (peak $4'$) shows a different intensity variation of the vibrational substates, revealing that they consist of two transitions, assigned to $Si\ 2p_{1/2} \rightarrow 4s$ and $Si\ 2p_{3/2} \rightarrow 4p$; the intensity

TABLE I. Summary of the present analysis of the Si 2p photoabsorption spectrum of SiCl₄: Assignments of the 2p → Rydberg excitations, resonance energies *E* (in eV) of transitions between lowest vibrational substates (*v''*=0 → *v'*=0), and quantum defects δ ; resonance energies marked by an asterisk are estimated from spin-orbit splitting.

<i>E</i>	$2p_{3/2}^{-1}$	$2p_{1/2}^{-1}$	δ
107.056	4s		1.89
107.661		4s'	1.88
107.939	4p		1.49
108.488	3d _e		0.09
108.507	3d _{i₂}		0.08
108.540*		4p'	1.48
109.088*		3d _e '	0.09
109.107*		3d _{i₂} '	0.08
109.201	4d		0.11
109.534	5d		0.09
109.698	6d		0.17
109.804		4d'	0.10
109.810*	7d		0.14
110.142		5d'	0.05
110.305		6d'	0.12
110.410		7d'	0.13
Threshold	110.099	110.688	

of the $2p_{1/2}^{-1}4s$ resonance amounts to less than half of that of the $2p_{3/2}^{-1}4s$ resonance. The resonances at $h\nu > 108.4$ eV (peaks 5, 5'; 6, 6') are due to $2p \rightarrow nd$ transitions, which are overlapping with a weak $2p_{1/2} \rightarrow 4p$ transition. A summary of the resonance energies (transitions between the lowest vibrational states, $v''=0 \rightarrow v'=0$), the quantum defects, and the adopted assignments of the Si 2p excitations is given in Table I. A detailed assignment of the *nd* excitations will be given further below.

IV. FRANCK-CONDON ANALYSIS

The high-resolution photoabsorption spectrum of SiCl₄ is obviously made up of overlapping spin-orbit-split electronic transitions and vibrational sidebands. Because of the regularity of the vibrational distances, only a single vibration with frequency ν_1 , namely, that of the symmetric-stretching vibrational mode, seems to contribute. This behavior is different from observations with SiH₄ [9] and CH₄ [5], where quite strong asymmetric vibrations were observed. It might be due to the larger size of the Cl ligand atom as compared to H, hindering sizable deviations from *T_d* symmetry, which would be required for strong excitations of asymmetric vibrations.

The easiest way to understand the vibrational structures is given by an analysis of the resonances in the energy range from 106.9 to 108.4 eV (see Fig. 2), where three Rydberg transitions ($2p_{3/2} \rightarrow 4s$; $2p_{1/2} \rightarrow 4s$; $2p_{3/2} \rightarrow 4p$) are involved, possibly overlapping with a weak valence transition at ≈ 107.5 eV (the latter is suggested by weak features in the photoabsorption spectrum of condensed-phase SiCl₄ [14]). The spectral structure from 106.9 to 107.6 eV is obviously caused by a single vibrationally

split Rydberg state, $2p_{3/2}^{-1}4s$. Here, the most intense peaks are those with higher vibrational quantum numbers *v'*, reflecting a large difference in equilibrium distances between the ground state and the core-excited state of SiCl₄; it is even difficult to identify the $v''=0 \rightarrow v'=0$ vibrational state. Moreover, due to the low ground-state vibrational energy of SiCl₄, $h\nu_g = 52.7$ meV [20], a substantial fraction of the molecules in the electronic ground state is expected to be vibrationally excited at room temperature, namely, 13% for $v''=1$ and 2% for $v''=2$, respectively. As usual, double-prime and single-prime vibrational states refer to the electronic ground state and the core-excited state, respectively.

The results of a detailed Franck-Condon analysis of the first three Rydberg resonances are given by the solid curves through the data points in Fig. 2 as well as by the solid subspectra. These Franck-Condon fits were carried out by assuming constant intrinsic widths and ground-state values of the vibrational energy of $h\nu_g = 52.7$ meV

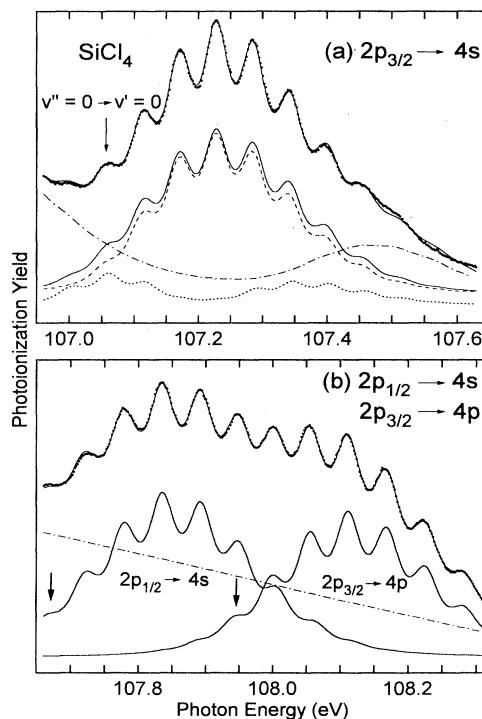


FIG. 2. Results of a detailed Franck-Condon analysis of the photoabsorption spectrum of SiCl₄: (a) in the region of Si $2p_{3/2} \rightarrow 4s$ excitation; (b) in the region of the Si $2p_{1/2} \rightarrow 4s$ and Si $2p_{3/2} \rightarrow 4p$ Rydberg resonances. The solid curves through the data points represent the results of Franck-Condon fits taking thermally excited states in the electronic ground state into account; the dashed spectrum is the result of a Franck-Condon analysis without such “hot bands” (for details, see text). The dotted line is the difference between the solid and dashed curves expanded by a factor of 2, i.e., it represents the influence of the “hot bands” on the photoabsorption spectrum. The vertical arrows mark the $v''=0 \rightarrow v'=0$ transitions. The dash-dotted subspectrum represents the background, which, in the case of $2p_{3/2} \rightarrow 4s$, contains in addition a valence-band structure at ≈ 107.5 eV.

[20] and of the Si-Cl equilibrium distance of $R_g = 2.019 \text{ \AA}$ [21] for SiCl_4 , as well as a vibrational temperature of 300 K. Figure 2(a) shows the results of our analysis in the region of the $2p_{3/2} \rightarrow 4s$ excitation. The lowest-energy peak at $h\nu = 107.00 \text{ eV}$ is assigned to a transition from the ground state, $v''=1$, to the excited state, $v'=0$; the second peak at 107.06 eV is due to a combination of $v''=0 \rightarrow v'=0$ and $v''=1 \rightarrow v'=1$ transitions; the third peak at 107.11 eV stems from the $v''=0 \rightarrow v'=1$ transition, combined with $v''=1 \rightarrow v'=2$, etc. Figure 2(b) shows the results of our analysis in the region of the $2p_{1/2} \rightarrow 4s$ and $2p_{3/2} \rightarrow 4p$ excitations. The parameters derived from the fits of all three states agree very well: For the core-excited states we obtain a Si-Cl equilibrium distance of $R_e = 1.953 \pm 0.003 \text{ \AA}$ and an intrinsic width of $\Gamma = 48 \pm 2 \text{ meV}$. Using

$$E = E_0 + h\nu_e(v + \frac{1}{2}) + h\nu_e x_e(v + \frac{1}{2})^2$$

for the energy levels of an anharmonic oscillator, the vibrations are characterized by $h\nu_e = 58.1 \pm 0.5 \text{ meV}$, an anharmonicity of $h\nu_e x_e = 0.12 \pm 0.05 \text{ meV}$. In our fit analysis, no anharmonicity in the ground state was assumed. Note that the anharmonicity, despite its small value, has a strong influence on the intensities of the high- v transitions; it also shifts the transition energy by $(v + \frac{1}{2})^2$. As a consequence, we can unambiguously conclude from the fit analysis that the equilibrium distance in the excited state is smaller than in the ground state, in agreement with the smaller value known for the $(Z+1)$ molecule PCl_4^+ (equilibrium distance $R_g = 1.97 \text{ \AA}$ [22]), as well as with general considerations on molecular contraction due to core excitation into nonbonding orbitals (see, e.g., equilibrium distances in core-excited H_2CO [3] and CH_4 [5]).

This is a confirmation of the influence of thermally populated vibrational states ($v'' > 0$) in the electronic ground state of a molecule ("hot bands") on an inner-shell photoabsorption spectrum. To demonstrate the difference, we show in Fig. 2(a) also the result of a simulation with the fitted values of R_e , ν_e , and Γ , but neglecting thermal excitations of vibrational modes (dashed subspectrum). The difference from the solid subspectrum (dotted curve) represents the contribution from these thermally populated vibrational states with $v'' > 0$. The $v'' \neq 0$ contributions are largest for low- v' and high- v' excitations: This is due to the fact that excitations with $v'' \neq 0$ are predominantly at the vibrational *inversion* points and $v''=0$ excitations predominantly at R_g , giving a change in Franck-Condon intensity from a distribution peaked at 107.22 eV ($v'=3$) for $v''=0$ to a distribution peaked at both 107.05 and 107.36 eV for $v'' \neq 0$, respectively.

The intrinsic width $\Gamma = 48 \text{ meV}$ is found to be much smaller than derived from previous spectra, which is due to the resolution of the vibrational fine structure in the present work. On the other hand, our result for Γ is still higher than the calculated value of 33 meV , obtained from the total valence-electron density at the Si center in SiCl_4 [10]. This difference may be due to the decrease in equilibrium distance in the excited state, which causes an

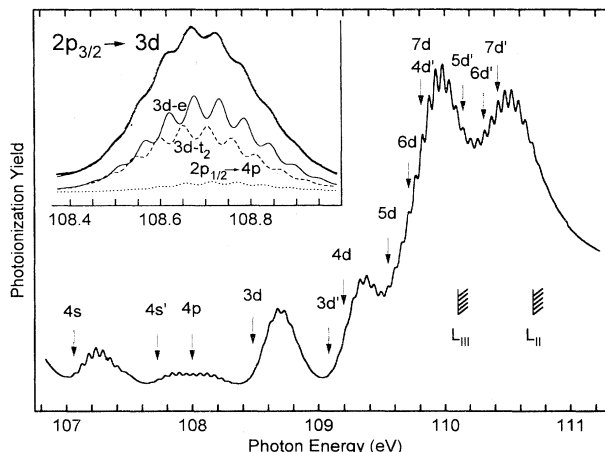


FIG. 3. Detail of the photoabsorption spectrum of SiCl_4 in the region of the $2p^{-1}4s$ to $2p^{-1}7d$ Rydberg excitations. The arrows mark the $v''=0 \rightarrow v'=0$ excitations on the basis of the given assignment (see text). The inset shows the result of a Franck-Condon fit of the vibrationally split $2p_{3/2}^{-1}3d$ Rydberg resonance assuming two resonances with equal and constant intrinsic widths, resulting in an $e-t_2$ splitting of 25 meV (solid and dashed subspectra); in addition, a weak $2p_{1/2}^{-1}4p$ Rydberg transition was added (dotted subspectrum).

increase of the electron density at Si.

The two following Rydberg transitions, $2p_{3/2}^{-1}3d$ and $2p_{1/2}^{-1}3d$, have much larger linewidths than all Rydberg states at lower as well as at higher energies: a fit gives a value of $\Gamma \approx 77 \text{ meV}$. This broadening is probably due to a ligand-field splitting of the $3d$ transitions into states with $3d e$ and $3d t_2$ symmetry, confirming the given assignment of the resonances. A fit of the $2p_{3/2}^{-1}3d$ resonance with two $3d$ series assuming $\Gamma = 48 \text{ meV}$ results in an $e-t_2$ splitting of 25 meV (see inset in Fig. 3). For both series, Franck-Condon parameters similar to those derived from the $4s$, $4s'$, and $4p$ Rydberg resonances at lower energies are obtained.

In the higher-energy region, the transitions are assigned to nd Rydberg states with nearly constant quantum defects (see Fig. 3 and Table I); they are again narrower than the $3d$ Rydberg states. This is readily understandable, since the $e-t_2$ splitting is expected to decrease with increasing n , i.e., it will be much smaller for $4d$, $5d$, etc. transitions. As a consequence, the vibrational fine structure is again distinctly observed. Also, there must be a coincidence of the number of vibrations, the spin-orbit splitting, and the difference of the most intense Rydberg states, in order to prevent a smearing out of the vibrations. Unfortunately, these Rydberg states exist on broad valence structures, which renders a Franck-Condon analysis that is based on the intensities of the vibrational states impossible. As a consequence, we have only marked in Fig. 3 by solid vertical arrows the $v''=0 \rightarrow v'=0$ transitions in the most probable assignment of the vibrationally split Rydberg states.

V. SUMMARY

The Si 2p photoabsorption spectrum of SiCl₄ recorded with high spectral resolution exhibits a vibrational fine structure of the $2p_{3/2}^{-1}4s$, $2p_{1/2}^{-1}4s$, $2p_{3/2}^{-1}4p$, $2p_{3/2}^{-1}nd$, and $2p_{1/2}^{-1}nd$ Rydberg states with a vibrational splitting of 58.1 meV. We obtain intrinsic widths of the Si 2p core-excitation resonances that are much narrower than reported in the literature up to now [10,12]. We have observed vibrational splitting in core-excited SiCl₄. Additionally, there is a thermal population of vibrationally ex-

cited states in the *ground* state of SiCl₄ at room temperature, which has to be taken into account in the Franck-Condon analysis of the core-excited spectrum.

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