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Si K-SHELL ABSORPTION SPECTRA OF CHLOROMETHYLSILANE MOLECULES IN THE GAS PHASE

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Résultes
Nous avons mesuré les spectres de photo absorption des molécules chloromethylsilane dans la région du seuil Si $1s$ (entre 1840 et 1900 eV) avec une très haute resolution et une statistique améliorée. Cette étude systématique facilite l'interprétation des résonances et devrait aider à comprendre l'environnement chimique donnant lieu à des résonances de forme.

Abstract
The photoabsorption spectra of the chloromethylsilane molecules $(\text{CH}_3)_n\text{SiCl}_{4-n}$ ($n=0$ - 4) have been measured near the Si $1s$ - edge (between 1840 and 1900 eV) with high resolution and improved statistics. This systematic investigation facilitates the interpretation of the observed resonances and is believed to help in the understanding of the chemical environment giving rise to shape resonances.

1. Introduction
Though recent theoretical /1,2/ and experimental /3/ results show promise of XANES being a new powerful structural technique, it should be pointed out that there are still several open questions. A final prove is still needed to show wether it is possible really to deduce a complete structure from a XANES spectrum. The best candidates for such an attempt are stable molecular gases for which their coordination geometries are well known from other experiments. Here, no perturbing effects are expected from non-next neighbour shells as for solids. In this paper we report our new high resolution spectra of the K - shell photoabsorption of silicon in simple chloromethylsilane molecules.

It is the main purpose of this contribution to demonstrate the advantages of systematic measurements for a consistent interpretation of the K - shell near edge structure. Thus we confine ourselves to a qualitative interpretation of spectra and observed systematic trends. A more detailed quantitative analysis of the data will be published in a following paper.

2. Experimental
Our measurements were carried out at the Bonn 2.5 GeV synchrotron running at 2.0 GeV with an electron current of about 20 mA /4/. A double crystal vacuum monochromator of the Lemmonier type /5/ was used equipped with InSb (111) crystals.

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giving an estimated resolution of about 0.5 eV in the energy region of interest. For all spectra a step width of about 0.1 eV was used. Our energy scale was calibrated against the white line of SF$_6$ (2485.9 eV) and/or against the well known white line of Argon at 3203.54 eV. By using both lines also the accuracy of the crystal constants used could be checked. The value used for our measurements was $2d_{\text{eff}}=7.48$ Å for InSb (111). The number of photons was about $10^9$ per resolution interval and second. Spectra were taken with the standard X-ray absorption technique. The monochromatized radiation is monitored by an ionisation chamber before passing the sample cell. A second ionisation chamber is used as a detector. The preamplified currents are given on VFCs which are read out by a VME-bus computer controlling also the scanning of the monochromator. The sample cell separated by kapton windows from the ionisation chambers is about 20 cm long. The pressure in the cell is varied between some tenths and about 50 Torr. The purity of the investigated molecules was in all cases higher than 99%.

3. Results and Discussion

As an example of our results, XANES spectra are shown in figure 1 of a series of molecules starting from SiCl$_4$ and going to Si(CH$_3$)$_4$ (TMS) by successively replacing a chlorine atom by a methyl group. The spectra are aligned at the Si IIs ionisation limits and thus are presented on a common term value scale. As some of the resonances above the ionisation limit are rather weak as compared to the resonances below the IP, the energy region above the IP is shown in figure 2 on an enlarged scale. Our spectra show clearly several systematic trends:

- As is expected, the ionisation potential is moving continuously down in energy from TMS to SiCl$_4$;
- With the ionicity increasing from TMS to SiCl$_4$, the term value of the resonances below the IP increases;
- In all spectra at least two distinct shape resonances are observed within 15 eV above the IP. The stronger one of these two features (at higher energies) has a term value which seems to be constant within our error margins for all molecules. The low energy resonance which is just a shoulder for TMS gains intensity when going to SiCl$_4$, ending with about the same intensity as the high energy resonance. This shape resonance changes its energy position and the corresponding term value decreases from TMS to SiCl$_4$, where the line is just at the ionisation limit. This observation of two shape resonances is believed to be characteristic for all tetrahedral molecules as was also demonstrated from multiple scattering calculations for GeCl$_4$ /1b/;
- For all molecules with Si bound to C as well as to Cl, two separated lines are
observed in the spectra below the IP. From systematic changes in intensity and energy, these lines can be assigned as to belong to a transition to an \((\text{Si-Cl})^m\) orbital and to an \((\text{Si-C})^m\) orbital, respectively, whereby the line with the larger term value corresponds to the transition to the \((\text{Si-Cl})\) orbital;
- by applying the bond length - energy correlation \(\Delta_{\text{R}} R^2 = \text{const.}\) as reported by Natoli /9/ we find fair agreement with theory when the \(\sigma^*\) resonance with the higher term value is correlated to the \(\pi^*(\text{Si-Cl})\) transition. For the low energy \(\sigma^*\) resonance such as correlation could not be proved;
- there are further resonances above the IP which are clearly seen in the \(\text{SiCl}_4\) spectrum in figure 2. The strongest of these structures decreases in intensity from \(\text{SiCl}_4\) to TMS where it could not be detected at all. Thus, a connection to the Cl-atom seems obvious but a definite interpretation is not yet possible;
- from the well resolved lines in the discrete part of the spectrum of \((\text{CH}_3)\text{SiCl}_3\) it is possible to obtain a reliable value for a Gaussian halfwidth. Based on this value all spectra were deconvoluted. It turned out that in all cases more lines were required than expected from the symmetries of the various ground states. This strongly supports an interpretation of the silicon halide spectra on the basis of a Jahn - Teller Effect as was reported by Bodeur et al. /6,7/.

The spectra of \(\text{SiCl}_4\) and \(\text{Si}(\text{CH}_3)_4\) were already reported before /6,7/ and our results are in good overall agreement with those data. However, statistics seems to be better in our data so that some finer details can be observed which were not reported in previous studies. The second rather weak shape resonance, for example, as observed in TMS about 4 eV above the IP, has not been seen before. This finding of a second shape resonance, however, is consistent with the data of the continuum structure above the Si 2s edge which were recently reported by Bozek et al. /8/.

There is another discrepancy in the spectrum of \(\text{SiCl}_4\) as compared to spectra reported by Bodeur et al. /6/. We observe a resonance just at the IP which was assigned before as a discrete state well below the IP. The position reported here is not only in agreement with the Si 2s spectrum of \(\text{SiCl}_4\) as reported by Bozek et al. /8/ but is also supported by the systematic trends as discussed above. It is assumed that this discrepancy is caused by an incorrect 2d - value used in the previous study and not by a wrong value for the ionisation potential as was suggested by Bozek et al. /8/.

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Figure 1: The Si K-shell XANES of Chloromethylsilane molecules

Figure 2: The Si K-shell absorption Spectrum of Chloromethylsilane molecules above the ionisation potential

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