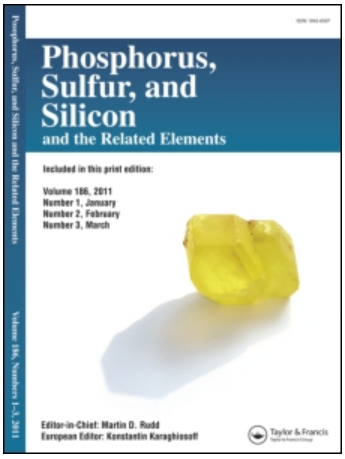

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INVESTIGATION OF P_4O_6, P_4O_{10} AND P_4O_6S BY X-RAY ABSORPTION SPECTROSCOPY AT THE PHOSPHORUS K-EDGE

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Abstract X-ray photoabsorption spectra at the phosphorus K-edge are reported for P_4O_6, P_4O_{10} and P_4O_6S molecules in the gas phase. The XANES region is shown to be very sensitive to the valency of the excited phosphorus atom and to the electronegativity of its nearest neighbour-atoms. By considering P_4O_6 and $(C_6H_5O)_3PS$ as reference models corresponding to the various chemical environments of phosphorus in the P_4O_6S-molecule, its XANES-spectrum can be represented as an additive superpositon of the P_4O_6- and the $(C_6H_5O)_3PS$-spectra. This indicates a localization of the different molecular orbitals in the corresponding parts of the molecule.

Phosphorus forms a series of molecular oxides and oxidesulphides with the general formula $P_4O_6X_n$ (X=O,S; n=0–4). Their structures can be derived from the basic P_4O_6-cage, which is similar to that of adamantane, by adding terminal oxygen or sulphur atoms to the phosphorus atoms. This process leads to different chemical valencies and to modifications in the local environment of the corresponding phosphorus atoms, as well as to geometrical changes of the whole basic P_4O_6-structure[1–3].

X-ray absorption near edge spectroscopy (XANES) is a sensitive probe of the valency, the coordination geometry, the symmetry of the unoccupied electronic states, and the effective charge of a chosen atom within a molecule, or in a solid[4]. As similar molecules have similar fine structures in the near edge region, information about certain molecules can be obtained by comparing XANES-spectra of appropriate reference compounds and using them as fingerprints.

XANES-spectra of P_4O_6, P_4O_{10}, P_4O_6S and $(C_6H_5O)_3PS$ have been obtained at the phosphorus K-edge using the synchrotron radiation beamline BN2 of the ELectron Stretcher Accelerator ELSA in Bonn, operating in storage mode at 1.9 GeV and with an average current of about 50 mA.[5]

After monochromatization by a double crystal monochromator of the Lemmonier type[6] equipped with two InSb(111) crystals, the beam passes through a reference ionization chamber, through the heatable sample chamber and finally through the detector ionization chamber. The absorption cross section was obtained by scanning the photon energy from 2130 eV to 2190 eV in steps of 0.03 eV with an integration time of 0.1 seconds per step, and by recording the logarithmic ratio of the currents of the reference and the detector chamber respectively. The measurements were carried out with the samples in the gas phase in order to avoid intermolecular interactions, hence they were vaporized by heating the sample chamber (P_4O_6: 30°C, P_4O_{10}: 200°C, P_4O_6S: 22°C).

Figure 1 presents the XANES-spectra of P_4O_6 (a), P_4O_{10} (b), P_4O_6S (c) and $(C_6H_5O)_3PS$ (d). Each spectrum was normalized at the maximum intensity. The low energy peaks (1-3 in (a) and (b); 1-2 in (c)) are assigned to electron transitions from 1s to unoccupied molecular orbitals below the ionization potential, whereas the so called shape resonances above the ionization energy (4,5) are due to multiple-scattering resonances in the continuum.[4,7] A detailed discussion of the XANES spectra of P_4O_6 and P_4O_{10} is given in a paper by Küper et al.[7].

A comparison of the XANES-spectra of P_4O_6 and P_4O_{10} first of all reveals the influence of the valence of the absorbing atom. The position of the absorption maxima are listed in table 1. It was found empirically that the energy position of the first strong resonance in the near-edge structure (white line) shifts to higher energies with increasing valency of the absorbing atom.[8,9] In this case the energy shift between the white lines in the absorption spectra of P_4O_6 containing P(III) and P_4O_{10} containing P(V) amounts to 4.3 eV. The calculated difference between the ionization potentials of the 1s electron in P_4O_6 and P_4O_{10} is 3.6 eV. Thus, the observed energy shift of 4.3 eV can be interpreted mainly as an influence of the different 1s ionization potentials.

Considering the XANES-spectrum of P_4O_6S, the first resonance (1) occurs at nearly the same energy as the corresponding resonance in the P_4O_6-spectrum. This agreement indicates a transition from 1s orbital of a phosphorus atom with valency III to a similar unoccupied molecular orbital in both compounds. Thus, this resonance can be assigned to a P(III) $1s \rightarrow \sigma^*$(P(III)-O) transition.

From the comparison of the energy position of resonance (2) of P_4O_6S with the spectrum of P_4O_{10} it is likely that this resonance is due to a transition from P(V) 1s. Hence, this transition can be assumed to be localized in the P(V)-O/P(V)-S part of the molecule. The observed shift between resonance (2) of P_4O_6S and

resonance (1) of P_4O_{10} is probably caused by the lower electronegativity of sulphur as compared with oxygen.

Due to the observed localization of the transition within the corresponding part of the molecule, $(C_6H_5O)_3PS$ seems to be a very suitable model compound for the "P(V)-part" of the P_4O_6S molecule as it contains the same PO_3S fragment. The P-1s-XANES-spectrum of this molecule is shown in figure 1d.

Following the above arguments, the absorption spectrum of P_4O_6S can be regarded in a first approximation as an additive superposition of the spectra of P_4O_6 and the PO_3S fragment available in the XANES-spectrum of $(C_6H_5O)_3PS$.

Adding the spectra of $(C_6H_5O)_3PS$ and P_4O_6, while shifting the latter about 0.4 eV to higher energies leads to the spectrum b) in figure 2, whereas a) presents the measured XANES-data of P_4O_6S. Considering the number of the absorbing P-atoms in each of the molecules, the P_4O_6-spectrum is weighted by a factor 0.75 before adding it to that of $(C_6H_5O)_3PS$. This reflects the ratio of the number of P(III) and P(V) atoms in the P_4O_6S molecule, which is 3:1.

The obvious similarity of the measured (a) and the simulated (b) P_4O_6S-spectrum strongly supports the assumption that the observed transitions can be localized within defined parts of the P_4O_6S molecule. The weighting factors used for the P_4O_6 and the $(C_6H_5O)_3PS$ spectrum respectively correspond nicely with the ratio of P(III)- and P(V)-atoms in P_4O_6S, while the shift to higher energies of the P_4O_6-spectrum can be interpreted as an influence of the slightly modified electron density at phosphorus (an influence of the P(V) in the second coordination shell) and small geometrical changes in the basic P_4O_6-structure.

The near-edge structures of P_4O_6, P_4O_{10} and $(C_6H_5O)_3PS$ will serve as standards for further investigation on phosphorus-oxides and -oxidesulphides.

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TABLE 1 Energy position of the resonances in P_4O_6, P_4O_{10}, P_4O_6S and $(C_6H_5O)_3PS$

No.	P_4O_6	P_4O_{10}	P_4O_6S	$(C_6H_5O)_3PS$
1	2147.44 eV	2151.7 eV	2148.0 eV	2150.2 eV
2	2149.7 eV	2153.51 eV	2150.6 eV	2152.0 eV
3	2152.09 eV	2154.76 eV	2155.5 eV	2159.0 eV
4	2153.99 eV	2158.1 eV	2166.5 eV	
5	2164.1 eV	2161.99 eV		

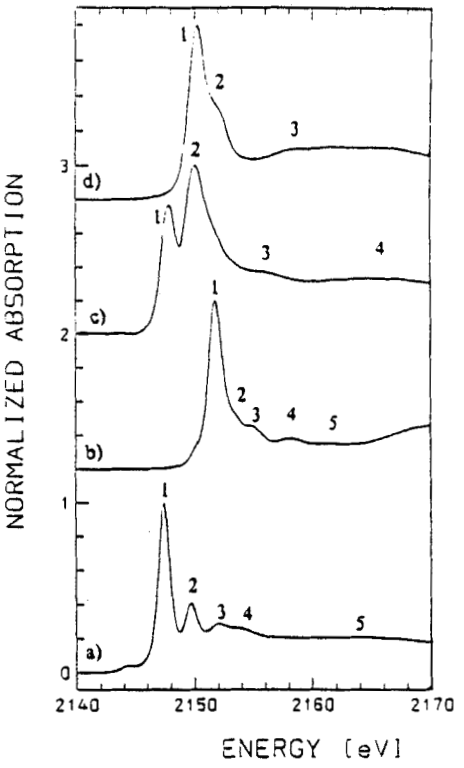

FIGURE 1
P K-edge absorption spectra of a) P_4O_6, b) P_4O_{10}, c) P_4O_6S and d) $(C_6H_5O)_3PS$, normalized to their maximum intensity

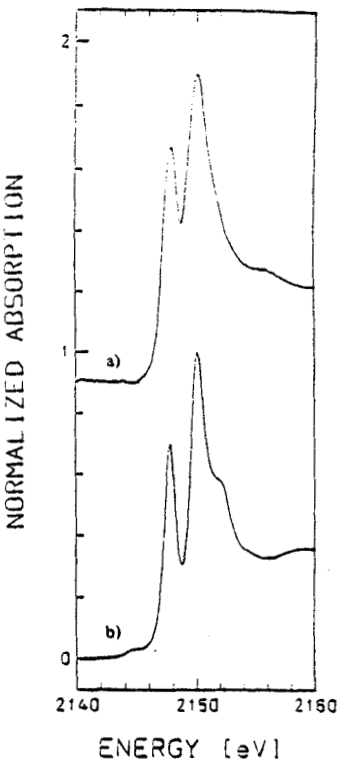

FIGURE 2
XANES-spectra of P_4O_6S, a) measured data, b) simulated spectrum by adding the P_4O_6-spectrum (weighting factor 0.75) and the $(C_6H_5O)_3PS$-spectrum (weighting factor 1)

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