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Investigations of $P_4O_6S_n$ ($n = 1-4$) by X-ray Absorption Spectroscopy at the P and S K-Edges

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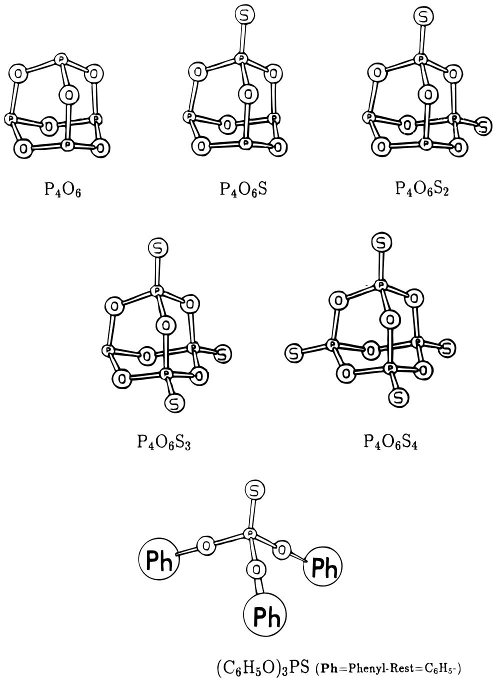
Abstract: X-ray absorption spectra at the P and S K-edges are reported for the molecules $P_4O_6S_n$ ($n = 1-4$) in the gas phase. The X-ray absorption near edge structure (XANES) region is shown to be very sensitive to the valency of the excited phosphorus atom. P_4O_6 and $(C_6H_5O)_3PS$ are used as reference compounds corresponding to the different chemical environments of phosphorus in the investigated phosphorus oxide sulfides. The XANES spectra of the phosphorus oxide sulfides can be represented by a superposition of the P_4O_6 and $(C_6H_5O)_3PS$ spectra. Using XANES as a fingerprint method, the single lines in the XANES region are assigned to molecular fragments. The results are compared with MS Xα calculations of the PO_3S cluster, which is assumed to contain all the interactions that are relevant for the P(V) portion in the molecules.

Introduction

The X-ray absorption near edge structure (XANES) can be used to investigate a selected element within a molecule or solid and at a chosen absorption edge, as well as to probe the local chemical environment of the excited atom. Especially at the K-edge of an absorbing atom, strong resonances appear below the ionization potential, and they are assigned to electron transitions from the 1s orbital to unoccupied electronic states below the ionization limit. Their number, the energy position, and the intensity of these resonances are very sensitive to the type and symmetry of the unoccupied electronic states. Hence, they are sensitive to the valency, the coordination geometry, and the effective charge of the absorbing atom. For this reason the near edge fine structure can be used for a qualitative analysis of the local environment of a particular atom in a molecule.[1,2] An advantage of XANES is that amorphous samples such as glasses and polymers can be investigated as well as crystals, since no long-range order is required in the samples. Moreover, the measurements can also be carried out with liquids, or samples in the gas phase.[3]

The motivation of this work was to study the relationships between electronic and structural properties of well-defined simple molecules, with the view of applying XANES results to more complex compounds. Since similar molecules are found to reveal similar fine structure in the near edge region, information about molecules of interest can be obtained by comparing their XANES spectra with spectra of appropriate reference compounds and thereby using the reference spectra as fingerprints.[3,4] With this in mind, the series of molecular phosphorus oxide sulfides $P_4O_6S_n$ ($n = 1-4$) seems to represent a suitable model system for such an investigation. Their chemical structures are well known from X-ray diffraction studies, and they can all be derived from the same basic P_4O_6 cage (Figure 1), simply by adding up to four terminal sulfur atoms to the phosphorus atoms. Apart from slight geometrical changes of the whole basic P_4O_6 cage, this addition leads predominately to modifications of the local environment of the corresponding phosphorus.[5−11] Whereas P_4O_6 contains four


P_4O_6 P_4O_6S $P_4O_6S_2$

$P_4O_6S_3$ $P_4O_6S_4$

$(C_6H_5O)_3PS$ (**Ph**=Phenyl-Rest=C_6H_5-)

Figure 1. Structures of the investigated molecules.

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formally equivalent trivalent P atoms, the equivalent P atoms in $P_4O_6S_4$ are all pentavalent. In the intermediate molecules P_4O_6S, $P_4O_6S_2$, and $P_4O_6S_3$ both P(III) and P(V) coexist in a varying ratio.

Hence, XANES spectra at the P and S K-edges of these molecules were obtained. Further, in order to study the influence of the first as well as higher coordination shells on the electronic properties of the absorbing atom, an additional XANES spectrum at the P K-edge of $(C_6H_5O)_3PS$ was measured. This molecule contains the same PO_3S fragment as the phosphorus oxide sulfides (Figure 1), and comparison with the XANES spectrum of this reference compound yields information about the degree of localization of the molecular orbitals at particular parts of the molecule.[12] The interpretation of the single lines in the XANES region is corroborated by MS Xα calculations of the PO_3S fragment present in the reference compound $(C_6H_5O)_3PS$.

Experimental Section

Experimental Details. The XANES spectra were obtained at the beamlines BN2 and BN3 using the synchrotron radiation of the Electron Stretcher Accelerator ELSA in Bonn, operating in storage mode at 1.9 GeV with an average current of about 50 mA.[14] The X-ray-beam is monochromatized by a double crystal X-ray monochromator of the Lemmonier type[15] equipped with two InSb(111) crystals. They have a 2d of 7.4806 Å and a resolution of 0.8 eV[16] at the P K-edge. The monochromatic photon flux rate is about 10^9 photons per second and per energy interval. The monochromatized beam first passes through a reference ionization chamber, then through a heatable sample chamber, and finally through the detector ionization chamber. In accordance with Lambert's law the absorption cross section can be obtained by recording the logarithmic ratio of the current of the reference and detector chambers as a function of the incoming photon energy. The photon energy was scanned from 2130 to 2190 eV at the P K-edge and from 2450 to 2510 eV at the S K-edge, in steps of 0.03 eV and with an integration time of 0.2 s per step. The experimental setup was calibrated to the maximum absorption of $Na_4P_2O_7$ (2152.4 eV) at the P K-edge and to the maximum absorption of $ZnSO_4$ (2481.44 eV) at the S K-edge. These substances have been chosen as energy standards because of their high chemical stability. The calibration could be reproduced with an accuracy of 0.05 eV. Higher orders were checked, and no influence was found. As the phosphorus oxide sulfides immediately decompose on exposure to air or moisture, a special sample chamber was constructed so as to keep the samples under an inert atmosphere (400 mbar of helium) during the measurements. In order to minimize intermolecular interactions, the measurements were carried out with the samples in the gas phase. Therefore, they were vaporized by heating the sample chamber (P_4O_6, 30 °C; P_4O_6S, 22 °C; $P_4O_6S_2$, 90 °C; $P_4O_6S_3$, 95 °C; $P_4O_6S_4$, 140 °C). The purity of the prepared samples was investigated by X-ray diffraction measurements and was found to be better than 99%.[5−11] Both before and after the XANES experiment, ^{31}P-NMR measurements of the samples were carried out to check that no decomposition or oxidation had taken place.

Data Analysis. In order to analyze the near edge region, a linear background due to L-shell absorption was subtracted from the raw data. After that the spectra were normalized to the absorption at 2190 eV. This enables us to directly compare the relative oscillator strengths of the various electron transitions. To extract information about single resonances within the near edge region, a least-squares fit of the XANES spectra at the P K-edge was made. The line shape of the resonances was assumed to be a Voigt profile, that is, a convolution of a Gauss function and a Lorentz profile. As the Gaussian line width represents the resolution of the monochromator, this parameter was set to a constant value of 0.9 eV. The Lorentz profile represents the natural line width, mainly caused by the lifetime of the electron hole. The fit was carried out so as to minimize the number of Voigt profiles within a fit, and thus the Lorentz width was set as a free parameter. Consequently, the fitted lines are sometimes quite broad, but this was done so as to select the strongest resonances. Especially near the ionization potential, the Lorentz width is found to increase. This might be due to several narrow lines overlapping, e.g., transition into Rydberg states. The absorption edge itself was represented by an arctangent function with the ionization potential at the turning point of this function.

The values of the ionization limits can be experimentally determined by X-ray excited photoelectron spectroscopy (XPS), but no 1s photoelectron spectra of gaseous $P_4O_6S_n$ (n = 0−4) have been published until now. However, some 1s and 2p photoelectron spectra of P_4O_6, P_4O_{10}, P_4S_{10}, $(CH_3O)_3PS$, and Na_3PO_3S exist.[17−19] The photoelectron energy of a particular compound is smaller in the solid than in the vapor phase, because the photoelectron loses kinetic energy while leaving the solid (work function). As the reported photoabsorption spectra were made with the samples in the gas phase, the 1s ionization energies of the vapor samples would be helpful for the data analysis, but only the 2p potential of P_4O_6 was measured in the gas phase.[20] As outlined by Küper et al.,[21] many 1s and 2p binding energies of gaseous phosphorus molecules[19,22−25] show a remarkable linear dependence between the 1s and 2p binding energies. Thus, the 1s ionization potential of P_4O_6 can be estimated from the 2p shift in accordance to the correlation[23] $\Delta E(2p) = 0.88\Delta E(1s) - 0.347$.

An ionization potential of 2153.7 eV was measured for P_4O_6,[21] and this value was used for this molecule as the energy position of the arctangent function, representing the ionization limit in the fit. With increasing P(V) portion in the molecules, the ionization potential is assumed to shift to higher energy, and this was also observed for the phosphorus oxide sulfides (Table 3).

MS Xα Calculation. Thari et al.[17] reviewed the MS Xα method, and in particular they pointed out its special usefulness in modeling the electronic structure of such phosphorus compounds as studied in this work. Details on the MS Xα program and the calculation method applied here have been presented in previous publications.[21,26]

The actual phosphorus oxide sulfide molecules are quite large and possess a relatively low symmetry. This symmetry is reduced further when the specific phosphorus atom that has been excited is explicitely taken into account. Therefore, not only would tackling this problem in a direct way by modeling the complete molecules in their various excited states require an excessive effort, but moreover the prospects for attaining a plausible picture through such a complex approach appear to be quite small. Thus, in the present study MS Xα calculations of the PO_3S cluster are reported. It represents a small constituent cluster of each of the phosphorus oxide sulfide molecules ($P_4O_6S_n$, n = 1−4). This PO_3S fragment is assumed to contain all the interactions that are relevant to the P(V) portion in the molecules. The structural data used in the calculation are listed in Table 1.

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Table 1. Structural Data Used in the MS Xα Calculation of the PO_3S Cluster

Bond Lengths (pm)	
P(V)−S	187.7
P(V)−O	161.1
Bond Angles (deg)	
S−P(V)−O	116.86
O−P(V)−O	101.20

Table 2. Weighting Factors of the Reference Spectra Used for the Simulated XANES Spectra

	reference spectrum	
simulated spectrum	P_4O_6	$(C_6H_5O)_3PS$
P_4O_6S	0.75	1
$P_4O_6S_2$	0.50	2
$P_4O_6S_3$	0.25	3

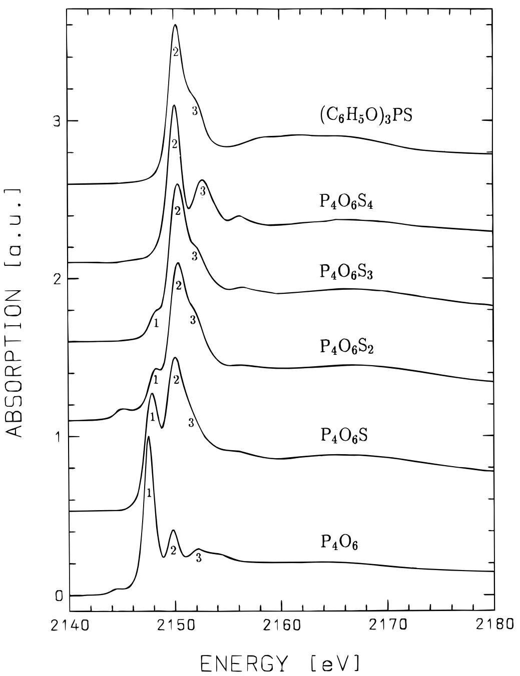

Figure 2. P K XANES spectra of the investigated molecules.

Results and Discussion

A Qualitative Discussion of the P K Near Edge Region. Figure 2 presents the XANES spectra of P_4O_6, P_4O_6S, $P_4O_6S_2$, $P_4O_6S_3$, $P_4O_6S_4$, and the reference compound $(C_6H_5O)_3PS$. For a better comparison of the relative oscillator strengths each spectrum in this figure is normalized to the maximum intensity. The lower energy peaks (1−3) are assigned to electron transitions from the 1s orbital to unoccupied molecular orbitals below the ionization potential, whereas the so-called shape resonances above the ionization energy not marked in the spectra are due to multiple-scattering resonances in the continuum.[1,21]

A comparison of the XANES spectra of P_4O_6, $P_4O_6S_4$, and $(C_6H_5O)_3PS$ first of all reveals the influence of the valency of the absorbing atom. It has been found empirically that the energy position of the first strong resonance in the near edge structure (the so-called white line) shifts to higher energies with increasing valency of the absorbing atom.[12,13,27,28] This is in good agreement with the spectra of P_4O_6 containing P(III) and of $P_4O_6S_4$ and $(C_6H_5O)_3PS$, both containing P(V). The energy shift between the white lines in the absorption spectra amounts to 2.6 eV.

Considering the XANES spectrum of P_4O_6S, the first resonance (1) occurs at nearly the same energy position as the corresponding resonance in the P_4O_6 spectrum. This agreement indicates a transition from the 1s orbital of a phosphorus atom with valency III to a similar unoccupied molecular orbital in both compounds. Hence, this resonance can be assigned to a P(III) 1s → σ^*(P(III)−O) transition.[21] Looking at the spectra of $P_4O_6S_2$ and $P_4O_6S_3$, a corresponding resonance (1) can be observed. In accordance with the decreasing P(III) portion in the molecules the intensity of resonance 1 declines and totally disappears in the $P_4O_6S_4$ spectrum, due to the lack of any P(III) atoms. These observations indicate a high degree of localization of the molecular orbitals at the P(III) atoms in each of the molecules. The remaining effect of delocalization, and the influence of the second coordination shell on the P(III) 1s → σ^*(P(III)−O) transition, can be observed in the slight shift of resonance 1 to higher energies with increasing P(V) proportion (P_4O_6, 2147.44 eV; $P_4O_6S_3$, 2148.2 eV), but this effect is comparatively small.

Considering the second resonance (2) in the P_4O_6S, $P_4O_6S_2$, and $P_4O_6S_3$ spectra, it is striking that they appear at nearly the same energy position as the white line (resonance 2) in the spectra of $P_4O_6S_4$ and $(C_6H_5O)_3PS$. This correspondence indicates that these resonances are due to equivalent electron transitions from the P(V) 1s orbital to similar unoccupied electronic states in each of the molecules. It also indicates a high degree of localization of the molecular orbitals at the corresponding P(V) atoms. However, in this case no influence of the second coordination shell (P(III)) can be observed. Furthermore, comparison of the spectra shows that $(C_6H_5O)_3PS$ is a suitable model compound for the P(V) part in the molecules, as it contains the same PO_3S fragment.

Simulated XANES Spectra of $P_4O_6S_n$ ($n = 1−4$). According to the arguments above, the absorption spectra of P_4O_6S, $P_4O_6S_2$, and $P_4O_6S_3$ can be regarded in a first approximation as a linear superposition of the PO_3 fragment (P(III)) available in the P_4O_6 spectrum and the PO_3S fragment (P(V)) available in the XANES spectrum of $(C_6H_5O)_3PS$. This can be achieved by simply adding the suitably weighted reference spectra of P_4O_6 and $(C_6H_5O)_3PS$. In order to retain the relative ratio of the resonance intensities, all spectra are usually normalized to a point far above the edge. Since the number of absorbing P atoms in the reference molecules is different—P_4O_6 has four P atoms, whereas the $(C_6H_5O)_3PS$ molecule only contains a single P atom—this must be taken into account in the weighting factors. Further, the weighting factors also reflect the ratio of the number of P(III) and P(V) atoms in the molecules, which is 3:1 in P_4O_6S, 2:2 in $P_4O_6S_2$, and 1:3 in $P_4O_6S_3$. The weighting factors necessary are listed in Table 2. In addition to this, the P_4O_6 spectrum has been shifted to higher energies by about 0.4 eV (P_4O_6S), 0.6 eV ($P_4O_6S_2$), 0.8 eV ($P_4O_6S_3$) in order to account for the influence of the second coordination shell. A striking similarity between the resulting constructed spectra and the actual measured absorption spectra can be observed in every case (Figure 3).

The observed localization of the resonances within the XANES spectra and the obvious similarity of the measured and simulated spectra strongly support the assumption that the observed transitions are localized within defined parts of the molecules. The weighting factors correspond nicely to the ratio of P(III) and P(V) atoms, while the shift to higher energies of the P(III) resonance can be attributed to a slightly modified

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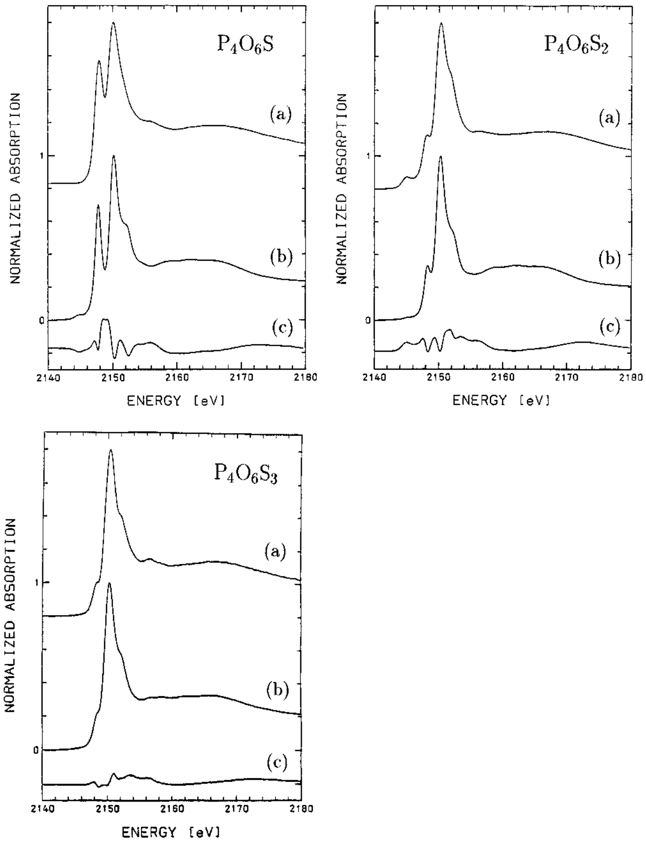

Figure 3. Simulated XANES spectra of P_4O_6S, $P_4O_6S_2$, and $P_4O_6S_3$: (a) measured data, (b) constructed spectrum, (c) difference between (a) and (b).

electron density at the absorbing P atom (an influence of P(V) in the second coordination shell) and to small geometrical changes in the basic P_4O_6 structure.

A More Detailed Discussion of the P K Near Edge Region and Comparison with the Results of the MS Xα Calculations. Looking at the XANES spectra of the investigated molecules (Figure 2), the absorption in the energy region above 2149 eV which corresponds to the P(V) part in the molecules is very broad. Obviously, this originates from a superposition of several narrow absorption lines that cannot be resolved. In order to obtain information about individual resonances within the near edge region, least-squares fits of the spectra have been made by using several Voigt profiles. The energy range between 2145 and 2160 eV of each P K XANES spectra is shown in Figure 4. The values of the ionization potentials (IP) obtained from the least-squares fits and the energy positions of the absorption maxima of the various resonances marked in Figure 4 and the Lorentz width obtained are listed in Table 3. A detailed discussion of the XANES spectrum of P_4O_6 is given in a paper by Küper et al.,[21] who assign resonance 1 to the transitions 1s → 5e and $5a_1$, which correspond to the P(III) part in the molecule.

Considering the P(V) component in the XANES spectra (energy region above 2149 eV), some new aspects now become obvious. The assignment of resonance 2 to an electron transition from the P 1s orbital to an unoccupied molecular orbital mainly localized at the P(V) atom and the terminal S atom is confirmed by MS Xα calculations of the PO_3S fragment, which models the P(V) part of the molecular phosphorus oxide sulfides. The results of the MS Xα calculations are depicted in the portion of Figure 4 showing the XANES region of the reference compound $(C_6H_5O)_3PS$. The transitions are assigned with increasing energy to the transitions 1s → $6a_1$, 6e, 7e, $8a_1$, and $9a_1$. Thus, resonance 2 can now be attributed to a transition from the 1s to the unoccupied molecular orbitals $6a_1$ and 6e. The calculated charge distributions of these orbitals reveal a high electron density in the P and S spheres. This localization and the particular l-type charge fractions in the P and S atoms furnish evidence that the transitions of 1s electrons into the $6a_1$ and 6e states can be attributed to the P═S bonding. Comparison with the P K XANES spectrum of P_4O_{10}[21] which contains four terminal P═O bondings, shows that the assignment of resonance 2 to an electron transition in a molecular orbital that is mainly built by P(V) and S is to be expected, since this resonance appears at a lower energy position (1.7 eV) than the corresponding absorption line in the P_4O_{10} spectrum (2151.7 eV[21]). Oxygen is more electronegative than sulfur, and it has been found empirically that increasing electronegativities of neighboring atoms tend to shift the resonances to higher energies.[13] By analogy, this assignment for resonance 2 also applies to the XANES spectra of the other molecular phosphorus oxide sulfides (Figure 4).

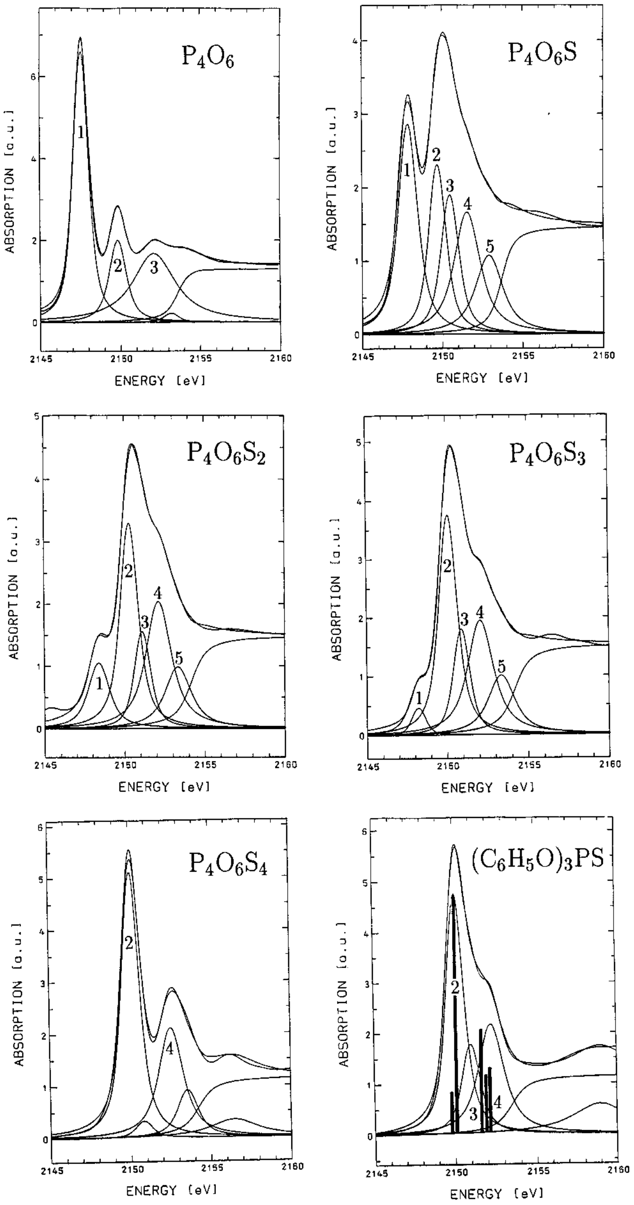

Figure 4. Least-squares fits for $P_4O_6S_n$ ($n = 0-4$) and $(C_6H_5O)_3PS$. The bold lines in the latter spectrum represent the results of the MS Xα calculations and are assigned with increasing energy to the transitions 1s → $6a_1$, 6e, 7e, $8a_1$, and $9a_1$.

Table 3. Results of the Least-Squares Fits Shown in Figure 4

	peak no.	energy (eV)	Lorentz width (eV)	absorption (arb units)	assignment
P_4O_6	1	2147.44	0.7	6.6	1s → P(III)—O
	2	2149.77	0.9	2.0	
	3	2152.09	3.1	1.7	
	IP	2153.70	0.9	1.3	1s → Kont
P_4O_6S	1	2147.87	1.1	2.9	1s → σ*(P(III)—O)
	2	2149.70	0.9	2.3	1s → σ*(P(V)═S)
	3	2150.48	0.9	1.9	
	4	2151.55	1.7	1.7	1s → σ*(P(V)—O)
	5	2152.90	1.8	1.1	
	IP	2153.70	0.9	1.5	1s → Kont
$P_4O_6S_2$	1	2148.07	1.2	1.0	1s → σ*(P(III)—O)
	2	2150.00	0.9	3.3	1s → σ*(P(V)═S)
	3	2150.80	0.7	1.5	
	4	2151.80	1.5	2.0	1s → σ*(P(V)—O)
	5	2153.00	1.6	1.0	
	IP	2153.90	1.2	1.5	1s → Kont
$P_4O_6S_3$	1	2148.23	0.5	0.5	1s → σ*(P(III)—O)
	2	2150.10	0.9	3.8	1s → σ*(P(V)═S)
	3	2150.91	0.7	1.8	
	4	2152.08	1.6	1.9	1s → σ*(P(V)—O)
	5	2153.35	1.6	1.0	
	IP	2154.20	1.2	1.5	1s → Kont
$P_4O_6S_4$	2	2150.05	0.9	5.1	1s → σ*(P(V)═S)
	4	2152.53	1.5	2.1	1s → σ*(P(V)—O)
	5	2153.57	1.2	0.9	
	IP	2154.30	1.3	1.1	1s → Kont
$(PhO)_3PS$	2	2150.08	0.9	4.7	1s → σ*(P(V)═S)
	3	2151.01	1.0	1.8	
	4	2152.25	1.6	2.2	1s → σ*(P(V)—O)
	IP	2153.50	1.3	1.2	1s → Kont

By comparing the relative intensities and energy positions, resonance 4 in the $P_4O_6S_4$ and the $(C_6H_5O)_3PS$ spectra seems to be caused by electron transitions, which possess analogous features. Since it appears at higher energy than resonance 2 (due to the P(V)═S part), this resonance is related to the P(V)—O part in the molecules, because of the higher value of the electronegativity of oxygen. Accordingly, resonance 4 can also be related to the P(V)—O portion in the XANES spectra of P_4O_6S, $P_4O_6S_2$, and $P_4O_6S_3$. It shifts slightly to higher energy (Table 3) with increasing P(V) content within the molecule, but this can be assigned to the electron-withdrawing tendency of the second neighbor shell. In the spectrum of P_4O_6 no such resonance 4 can be observed, which is expected because of the lack of any P(V) atom in the molecule. This interpretation is also corroborated by the results obtained from the MS Xα calculation of the PO_3S fragment. Resonance 4 in the $(C_6H_5O)_3PS$ spectrum can be attributed to the electron transition 1s → $8a_1$, and as indeed expected, the calculated l-type charge fractions of the $8a_1$ orbital indicate a corresponding localization at the P(V) and O atoms.

The similarity of the P(V) portion in the $P_4O_6S_3$ and $(C_6H_5O)_3PS$ spectra is striking. The intensities and the energy positions of the resonances are nearly identical. In comparison to the $P_4O_6S_4$ spectrum, resonance 4 which is related to the P(V)−O part is shifted slightly to lower energy (0.5 eV) in the $P_4O_6S_3$ spectrum. This can obviously be traced back to the influence of the second coordination shell, i.e., the increasing P(III) part in the molecule. An inspection of the $P_4O_6S_2$ spectrum discloses the same trend.

In the P_4O_6S molecule only one P(V) atom exists, in contrast to the three formally trivalent P atoms. The total intensity at the energy region above 2149 eV (which is mainly related to the P(V) part) is comparatively high, indicating a relatively high oscillator strength of the pertinent electron transitions. Nevertheless, strong resonances that are due to electron transitions from P(III) 1s to unoccupied molecular orbitals mainly built by P(III) and O are also expected to be above 2149 eV. As the fits have been carried out with the aim of detecting only the strongest resonances, it is not surprising that the fitted lines in the P_4O_6S spectrum possess different relative intensities than those in the $P_4O_6S_2$ and $P_4O_6S_3$ spectra. Besides, their energy positions have changed. Compared to $P_4O_6S_2$, resonances 2−4 are shifted about 0.3 eV to lower energy (Table 3).

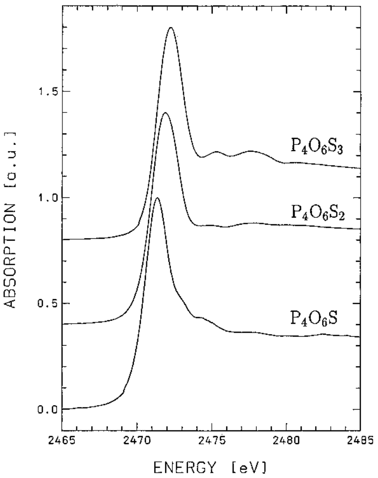

Figure 5. S K XANES spectra of $P_4O_6S_n$ (n = 1−3).

Finally , P_4O_6 does not contain any P(V) atoms, and hence, the respective absorption spectrum is totally different. In particular resonances 2 and 3 do not correspond to resonances in the phosphorus oxide sulfide molecules. According to Küper et al.,[21] they were assigned to P(III) 1s → σ*(P−O) electron transitions.

Thus, with increasing P(V) portion in the molecules resonance 1 (P(III)—O) decreases in intensity, is shifted to higher energies, and totally disappears in the spectrum of $P_4O_6S_4$, where no P(III) part is present. On the other hand, resonance 4 (P(V)—O) is shifted to lower energies with increasing P(III) part in the molecules, whereas resonance 2 related to the P(V)═S part exhibits no significant energy shift.

Discussion of the XANES Spectra at the S K-Edge. The sulfur atoms in the molecules $P_4O_6S_n$ (n = 1−4) are always terminally bonded to one of the phosphorus atoms in the basic P_4O_6 cage. If one also considers the three neighboring oxygen atoms in the P_4O_6 cage, the sulfur can in a first approximation be regarded as being at the top of a regular trigonal pyramid with phosphorus in the center and oxygen at the base. In doing so, one disregards the results of structure analysis by X-ray diffraction methods,[5−11] which discloses slight geometrical changes in the basic P_4O_6 cage and minor P═S bond length variations: 189.0 pm (P_4O_6S), 188.5 pm ($P_4O_6S_2$), 188.2 pm ($P_4O_6S_3$), 188.6 pm ($P_4O_6S_4$).[10]

Figure 5 presents the XANES spectra of P_4O_6S, $P_4O_6S_2$, and $P_4O_6S_3$ at the S K-edge. It appears quite plausible that the differences in the otherwise similar XANES spectra result from the slight geometrical changes in the representative PO_3S cluster. In all cases a dominant resonance is followed by two weaker absorption lines at about 2475 and 2478 eV. Analyzing the energy positions of the intense main resonance for the various systems discloses an energy shift to higher energies with increasing sulfur content (P_4O_6S, 2471.35 eV; $P_4O_6S_2$, 2471.85; eV; $P_4O_6S_3$, 2472.24 eV). In principle, both the slight P═S bond length variation and the varying content of pentavalent P in the P_4O_6 cage could cooperate in causing this observed energy shift. In order to discriminate between these two possibilities, preliminary calculations were carried out with the model cluster PO_3S with (i) varying P═S bond length and (ii) the three peripheral O atoms slightly charge-depleted in O 1s. The latter charge depletion was introduced in order to simulate the effective electron affinity of the outer surroundings which increases with increasing pentavalent P atom content. The results of these calculations lead us to conclude that the P valency prevails in producing the observed energy shifts of the main absorption line.

Conclusion

The molecular phosphorus oxide sulfides $P_4O_6S_n$ ($n = 1-4$) represent suitable model systems for demonstrating the usefulness of XANES measurements for investigating the local environment of a particular element within a molecule, if appropriate reference compounds are available. Using XANES as a qualitative fingerprint method, information can be obtained about the valency of the absorbing atom (P(III), P(V)). By regarding the P K near edge structures as an additive superposition of the reference spectra of P_4O_6 and $(C_6H_5O)_3PS$, the number of trivalent and pentavalent P atoms can be determined. These results are in good agreement with the actual P(III) and P(V) portions in each of the molecules. The least-squares fits of the XANES spectra by using a minimal number of Voigt profiles allow an assignment of individual lines to specific parts of the molecule (P(III)—O, P(V)═S, P(V)—O) and indicate a high degree of localization of the molecular orbitals within confined subregions of the phosphorus oxide sulfides. These assignments are corroborated by MS Xα calculations of the PO_3S fragment, which represents the P(V) portion in the molecules $P_4O_6S_n$ ($n = 1-4$) and in the reference compound $(C_6H_5O)_3PS$. The effect of the second coordination shell manifests itself mainly in causing only slight changes in the energy positions of certain lines. The results obtained by analyzing the P K near edge region agree with the corresponding XANES spectra at the S K-edge. As the results have been supported by MS Xα calculations, a semiquantitative picture of the XANES spectra of the complex phosphorus oxide sulfides has been obtained.

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