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OXYGEN K-SPECTRA AND ELECTRONIC STRUCTURE OF THE OXYANIONS SO_3^{2-}, SeO_3^{2-}, TeO_3^{2-} AND SO_4^{2-}, SeO_4^{2-}, TeO_4^{2-}

by

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Abstract

The oxygen K-emission spectra of the oxyanions SO_3^{2-}, SeO_3^{2-}, TeO_3^{2-} and SO_4^{2-}, SeO_4^{2-}, TeO_4^{2-} are reported. From the O K-spectra together with the complementary X-ray emission and photoelectron spectra aligned on a common energy scale one can build up a consistent picture of the electronic structure of these oxyanions. The orbital energies and the relative O 2p population of the orbitals are compared with theoretical predictions.

1. Introduction

In two previous papers we have reported on X-ray spectroscopic studies of the oxyanion PO_4^{3-} (1) and the oxyanions NO_2^-, NO_3^- and CO_3^{2-} (2). It has been demonstrated that if all X-ray emission spectra of the different atoms of an ion are measured, with the additional information from photoelectron spectra and theoretical MO-calculations, a rather accurate description of the electronic structure of the occupied molecular orbitals can be obtained.

The structural features of the different spectra permit a relatively precise determination of the binding energies of the orbitals which then can be used to check the predictions of theoretical MO-calculations. Since X-ray transitions are governed by the dipole selection rule, the intensities of the structural features in different X-ray emission spectra provide information as to what extent the individual atomic orbitals do contribute to the molecular orbitals.

In the present paper we report on similar investigations of the pyramidal anions SO_3^{2-}, SeO_3^{2-} and TeO_3^{2-} (C_{3v}) and the tetrahedral anions SO_4^{2-}, SeO_4^{2-} and TeO_4^{2-} (T_d). We have measured the O K-emission spectra of these oxyanions. The O K-spectrum reflects the relative amount of the O 2p component which contributes practically to all molecular orbitals of the anions. To determine the energy positions of the orbitals precisely, we use in addition to the O K-spectra the complementary X-ray and photoelectron spectra measured recently by other authors or those that appear particularly reliable. It is helpful for the interpretation of the spectroscopic data that within each of the two groups of divalent oxyanions the central atoms belong to the same group of the Periodic Table. Therefore, within each group of oxyanions similarities of the electronic structure and systematic changes of the shape of the spectra are to be expected. This provides additional support to establish the electronic structure also in cases where no theoretical predicitons are available.

2. Experimental

The O K-spectra were excited in fluorescence using the synchrotron radiation of the storage ring DORIS at Hamburg. The measurements were made on a 2 m concave grating spectrometer which has been described elsewhere (3). All the spectra were obtained using a step-scanning technique. The polycrystalline samples were cooled with liquid nitrogen. The angle between the direction of emission and the sample surface (= take-off angle) was about 9°. The spectral resolution was approximately 0.5 eV.

3. The O K-spectra of the pyramidal ions SO_3^{2-}, SeO_3^{2-} and TeO_3^{2-}

The O K-spectra of the pyramidal ions SO_3^{2-}, SeO_3^{2-} and TeO_3^{2-} (C_{3v}) have been measured for the first time. The spectra are presented in Fig. 1. By separate measurements the relative energy positions of the three spectra were determined with an accuracy of 0.1 eV.

As can be seen, the spectra are similar on the whole but differ in details. The positions of the structural features are denoted by capital letters. The broken lines under the experimental curves indicate locations and relative intensities of the resolved component peaks. The results are summarized in Table 1 (features $I_{exp.}$). We note that the relative intensities of corresponding structural features are of similar magnitude, but the positions of some peaks with the same designation change systematically.

The ion SO_3^{2-}

The sulfite ion has been studied most extensively both theoretically (4-8) and experimentally (8-19). In addition to the O K-spectrum, the S Kβ-spectrum (13-17), the S $L_{2,3}$-spectrum (8, 18, 19) and X-ray photoelectron spectra (9-12) are available.

In Fig. 2 the O K-spectrum measured for Na_2SO_3 together with the S $L_{2,3}$-spectrum of Na_2SO_3 (8) and the S Kβ-spectrum of K_2SO_3 (14) are shown. The energy positions of structures in the S $L_{2,3}$-spectrum actually refer to structures in the L_3-spectrum. These energies were determined after the L_2-spectrum had been subtracted from the S $L_{2,3}$-spectrum assuming the intensity ratio of L_2 and L_3 to be 1:2, and spin-orbit splitting to be 1.2 eV.

In the upper part of Fig. 2 the X-ray photoelectron (XP) spectrum measured for Li_2SO_3 (12) is shown. At the top, the theoretical results of a MO-calculation (8) are added.

All spectra have been aligned to a common energy scale considering the width and position of structural features and also the calculated population of the atomic components of the valence orbitals. For details of the correlation of the different individual energy scales see Ref. 1 and 2.

From the aligned spectra eight common structures are obtained - indicated by vertical lines - which are correlated with molecular orbitals. The high energy structures A and A' in the O K-spectrum (Fig. 1) cannot be attributed to molecular orbitals. These structures may be caused by absorption structure or by high energy satellites. It is also impossible to identify the structures at about 152 eV and 164 eV in the S $L_{2,3}$-spectrum with molecular orbitals (Fig. 2). As to orbital 3e, the calculated S 3p population (0.48) is considerably higher than expected from the intensity in the S Kβ-spectrum at about 2471 eV.— It should be mentioned that there are a number of discrepancies between the molecular orbital interpretation of other authors and the present interpretation based on more complete spectroscopic data.

The binding energies of the orbitals as determined from the entirety of the aligned spectra are listed in Table 1. For O 1s a binding energy of -531.5 eV is obtained, in good agreement with -531.9 eV (20) and -531.8 eV (11) resulting from XPS measurements. The binding energy of the S L_3-level is -167.1 eV; the value obtained by Narbutt (16) is smaller by 0.75 eV (-166.35 eV). For the S K-level the resultant binding energy is -2477.2 eV; in this case Narbutt's value (using the binding energy of the S L_3-level and the energy of the S $K\alpha_{1,2}$-lines) is considerably smaller (-2475 eV). This comparatively large discrepancy may have different causes which, however, may not be due to the alignment of the various spectra.

As can be seen from Table 1, the relative intensities of the structural features of the O K-spectra on the whole are in satisfactory agreement with the calculated O 2p populations. The calculated O 2p component in the orbital 1e is zero. The observed intensity of the corresponding feature is indeed small, but clearly measurable and even more intense than the O 2p component of orbital $1a_1$.

The ions SeO_3^{2-} and TeO_3^{2-}

For the oxyanions SeO_3^{2-} and TeO_3^{2-} up to now only the XP-spectra measured by Nefedov et al. (11) were published. Samples of $Li_2SeO_3 \cdot H_2O$ and Li_2TeO_3 were used; their spectra are shown in Figs. 3 and 4, respectively. The XP-spectrum of water-free Na_2SeO_3 measured by Hayes (21) is in good agreement with the spectrum of Fig. 3, except for the region of the O 2s orbitals, where it is disturbed considerably by the Na 2p photoelectron lines. The O K-spectra shown in Figs. 3 and 4 were obtained using samples of waterfree Li_2SeO_3 and Li_2TeO_3. The energy positions of the features and their estimated errors are listed in Table 1.

The alignment of the O K- and the XP-spectra in Figs. 3 and 4 is based only on the features of the spectra, because no further spectroscopic results are available. The binding energies obtained by this alignment are listed in Table 1. The binding energies for O 1s in SeO_3^{2-} and TeO_3^{2-} are -530.6 eV and -530.3 eV, respectively. These values are in close agreement with those reported by Nefedov et al. (11) (-530.9 eV and -530.3 eV). This agreement confirms the coordination of the spectra.

Up to now no MO-calculations for these oxyanions are available. The identification of the valence orbitals was based on the similarity of the O K- and also of the XP-spectra of the three pyramidal oxyanions, together with the electronic structure of the SO_3^{2-} ion as determined in the previous section. From the O K-spectra, information is obtained in particular about the region of the outermost orbitals. The shoulder at about 520.5 eV which shows up in the O K-spectra of all three ions (and which has no analogue in the XP-spectra) is to be attributed to the orbital $3a_1$. With the help of the X-ray spectra a better localisation is obtained for the four outermost orbitals than with the XP-spectra alone, the orbitals 4e and $1a_2$, however, cannot be resolved.

The positions of the more tightly bound orbitals of the three oxyanions are well defined by the XP-spectra (Figs. 2, 3 and 4). With increasing atomic number of the central atom the spacing between the O 2s orbitals decreases.

The similarity between the intensity distributions of the O K-emission spectra (Fig. 1, Table 1) shows that the valence orbitals of the ions SeO_3^{2-} and TeO_3^{2-} have about the same composition as those of the ion SO_3^{2-} at least as far as the O 2p components are concerned.

4. The O K-spectra of the tetrahedral ions SO_4^{2-}, SeO_4^{2-} and TeO_4^{2-}

The O K-spectra of the ions SO_4^{2-}, SeO_4^{2-} and TeO_4^{2-} are presented in Fig. 5. The energies of the structural features and the experimentally determined relative intensities are listed in Table 2. In a separate measurement the positions of the three spectra relative to each other were determined with an accuracy of 0.1 eV.

The shape of the spectra and the energies of structures D, B, A and A' change systematically from SO_4^{2-} to TeO_4^{2-}. The similarity of the shapes and their systematic change facilitate the interpretation of the results.

The ion SO_4^{2-}

The electronic structure of the sulphate ion has been the subject of several investigations. Dolenko et al. (22, 23) have measured all X-ray emission spectra applying fluorescence excitation, and correlated these spectra with one another and with the XP-spectrum (9, 24) using the binding energies of the core levels and the energy of the S $K\alpha_1$-line. Since these authors have not measured the spectra in their whole energy range and only with low resolution, it seemed worthwhile to retreat the electronic structure with spectra better resolved and measured over the whole energy range.

In Fig. 6 are shown the O K-spectrum of Li_2SO_4 measured in the present investigation together with the S $K\beta$-spectrum of K_2SO_4 (25) and the S $L_{2,3}$-spectrum of Na_2SO_4 (26). To correlate the spectra with one another the energies of the structural features of the L_3-spectrum were used. Also shown in Fig. 6 are an XP-spectrum (12) and UP-spectra (7) of Li_2SO_4. The UP-spectrum (He II) resembles the O K-spectrum since in UPS predominantly the p-components are reflected, and because the O 2p population is much higher than the S 3p population and concentrated upon the upper orbitals.

For the sulphate ion numerous MO-calculations have been performed (5, 6, 9, 15, 27-32) part of which exhibit considerable differences. Of all these calculations the one by Johansen (27) agrees best with the distribution of the orbitals and therefore is used in Fig. 6.

From the spectra aligned to a common energy scale we obtain for the SO_4^{2-} ion seven different energy states which can easily be identified (Table 2). Because of the T_d-symmetry of the ion, transitions to the S K-level occur only from three t_2 orbitals. The corresponding structural features are reflected in the S Kβ -spectrum.

The other four orbitals were identified with the help of the MO-calculations. As to the intense structures of the spectra, our interpretation of the spectra agrees with that of Dolenko et al. (22). The energies of the orbitals, however, could be determined more accurately. The binding energies are listed in Table 2. A satisfactory agreement is found between the intensities of peaks in the O K-spectra (Fig. 5) and the calculated O 2p components of the valence orbitals (Table 2).

From the spectroscopic data the binding energies of the following core-levels were also determined: -533.2 eV for O K, -169.8 eV for S L_3, and -2479.6 eV for S K. These values are in good agreement with XPS-results (20): -532.9 eV for O K and -169.3 eV for S L_3. The binding energy of the S K level as determined from the binding energy of S $L_{2,3}$ (-168.9 eV) (20) and the energy for the S K$\alpha_{1,2}$-lines (2309.0 eV) (23) is -2477.9 eV. This value is by 1.7 eV smaller than the value determined from the present results.

The ions SeO_4^{2-} and TeO_4^{2-}

For the ion SeO_4^{2-} only the X-ray photoelectron spectrum of $Li_2SeO_4 \cdot H_2O$ measured by Nefedov et al. (11) is available. In the present study the O K-spectrum of a sample of water-free Li_2SeO_4 was measured. The two spectra are shown in Fig. 7.

MO-calculations have been carried out by Höjer et al. (32) and by Shchegolov and Dyatkina (33). The results of the latter authors are shown at the top of Fig. 7.

The O K-spectrum of SeO_4^{2-} is interpreted by utilizing its XP-spectrum (11) and considering also the O K-spectrum of SO_4^{2-}. The positioning of the orbitals and their binding energies are presented in Fig. 7 and Table 2, respectively. The three outermost orbitals 1e, $3t_2$ and $1t_1$ are to be identified with the main peak of the O K-spectrum, and the orbital $2t_2$ corresponds to the peak at about 522 eV. The small width of the main peak of the O K-spectrum indicates that the spacings between the three outermost orbitals are smaller than the values predicted by theory (33).

The intensities of the structures of the O K-spectrum agree satisfactorily with the calculated O 2p components of the corresponding valence orbitals (Table 2). The resultant binding energy of O 1s is -532.1 eV which is identical with the result obtained by Nefedov et al. (11).

The O K-spectrum of TeO_4^{2-}, for which up to now neither experimental nor theoretical results are available, was measured using a sample of Li_2TeO_4. The positions of the orbitals, obtained by comparing the O K-spectra of SO_4^{2-}, SeO_4^{2-} and TeO_4^{2-} (Fig. 5) are listed in Table 2, together with the experimentally determined intensities. Since the intensity distributions of the O K-spectra of the three oxyanions with tetrahedral symmetry are similar, it follows that the composition of the valence orbitals - at least as far as the O 2p components are concerned - in the ion TeO_4^{2-} is similar to that of the two other oxyanions.

Acknowledgments

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Tab. 1: SO_3^{2-}, SeO_3^{2-}, TeO_3^{2-}: molecular orbitals (MO), notation (N), energy values of corresponding features in the O K-spectrum in eV (features), observed binding energies in eV (BE), observed relative intensities in the O K-spectra (I_{exp}) and calculated relative atomic 2p-components (theory) (8).

		SO_3^{2-}				SeO_3^{2-}			TeO_3^{2-}		
MO	N	features	BE	I_{exp}	theory	features	BE	I_{exp}	features	BE	I_{exp}
	A'	537.2±0.8		0.6		536.7±0.8		0.6	535.8±1		0.9
	A	530.7±0.6		3.8		530.6±0.6		3.3	530.5±0.7		4.7
$4a_1$	B	526.6±0.3	-4.6±0.3	54	44.9	526.7±0.3	-3.8±0.3	75	526.8±0.3	-3.5±0.3	71
$4e, 1a_2$	C	526.2±0.2	-5.7±0.3			525.8±0.2	-4.7±0.2		525.7±0.2	-4.6±0.2	
3e	D	524.5±0.2	-6.4±0.3	19	20.8	524.9±0.2	-5.6±0.3		524.6±0.2	-5.7±0.3	
2e	E	521.9±0.3	-9.7±0.2	10	20.5	521.9±0.2	-8.6±0.2	11	522.6±0.3	-7.9±0.3	13
$3a_1$	F	520.5±0.3	-10.7±0.2	6	9.2	520.3±0.3	-10.2±0.5	6	520.9±0.3	-9.4±0.5	5.5
$2a_1$	G	518.1±0.5	-13.3±0.7	3.5	4.3	516.8±1	-14.0±0.3	2.4	518.0±0.5	-13.1±0.3	3.5
	G'	514.5±0.7	-	1.0	-	-	-	-	-	-	-
1e	H	507.7±0.5	-24.2±1	1.3	0	509.0±1.5	-23.5±1	0.9	509 ±1.5	-22.8±1.5	0.9
$1a_1$	I	503.3±0.7	-28.2±1	0.7	0.3	504.5±1.5	-26.2±1	0.8	505 ±1.5	-23.8±1.5	0.5

Figure Captions

Fig. 1: O K-emission spectrum of SO_3^{2-}, SeO_3^{2-} and TeO_3^{2-}.

Fig. 2: O K-emission spectrum of SO_3^{2-} together with S Kβ-spectrum (14), S $L_{2,3}$-spectrum (8), X-ray photoelectron spectrum (12), and calculated electronic structure (8).

Fig. 3: O K-emission spectrum of SeO_3^{2-} together with X-ray photoelectron spectrum (11) and experimentally determined orbitals.

Fig. 4: O K-emission spectrum of TeO_3^{2-} together with X-ray photoelectron spectrum (11) and experimentally determined orbitals.

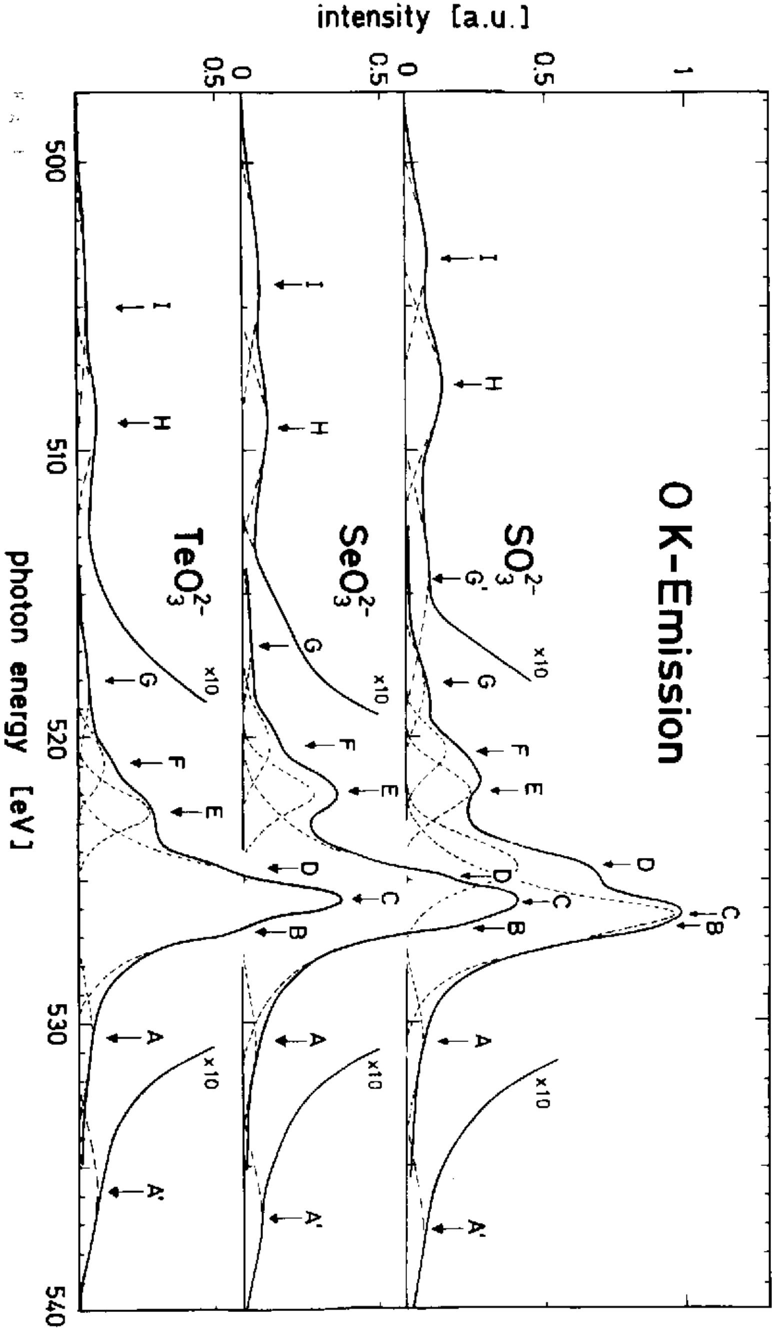
Fig. 5: O K-emission spectrum of SO_4^{2-}, SeO_4^{2-} and TeO_4^{2-}.

Fig. 6: O K-emission spectrum of SO_4^{2-} together with S Kβ-spectrum (25), S $L_{2,3}$-spectrum (26), X-ray photoelectron spectrum (12), UP-spectra (7) and calculated electronic structure (27).

Fig. 7: O K-emission spectrum of SeO_4^{2-} together with X-ray photoelectron spectrum (11) and calculated electronic structure (33).

Tab. 2: SO_4^{2-}, SeO_4^{2-}, TeO_4^{2-}: molecular orbitals (MO), notation (N), energy values of corresponding features in the O K-spectrum in eV (features), observed binding energies in eV (BE), observed relative intensities in the O K-spectra (I_{exp}) and calculated relative atomic 2p-component (theory) for SO_4^{2-} (27) and SeO_4^{2-} (33).

		SO_4^{2-}				SeO_4^{2-}				TeO_4^{2-}	
MO	N	features	BE	I_{exp}	theory	features	BE	I_{exp}	theory	features	I_{exp}
	A'	539 ±1		0.4	-	-				536 ±1	0.4
	A	531 ±1		6	-	530.5±0.8		8	-	529.5±0.7	6
$1t_1$	B	526.5±0.2	-6.6±0.2			526.0±0.2	-6.1±0.3			525.7±0.1	
$3t_2$			-8.4±0.3	76	74.7		-6.7±0.3	72	85.2		74
	C	524.8±0.2				524.8±0.3				524.6±0.3	
1e			-9.2±0.4				-7.2±0.3				
$2t_2$	D	521.2±0.2	-12.2±0.3	13	19,1	521.7±0.2	-10.4±0.2	14	12.2	522.0±0.3	15
$2a_1$	E	518.3±0.2	-14.8±0.2	3	4.3	518.0±0.7	-14.4±0.3	4	1.6	518.0±0.8	3
$1t_2$	F	507.5±0.8	-26.0±0.5	1	1.2	508.0±1	-24.1±0.4	1.3	0.6	507.7±1.5	1
$1a_1$	G	503.5±0.8	-30.0±1	0.5	0.7	503.5±1	-27.4±0.5	0.7	0.5	502 ±1.5	1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SeO$_3^{2-}$
TeO$_3^{2-}$
A
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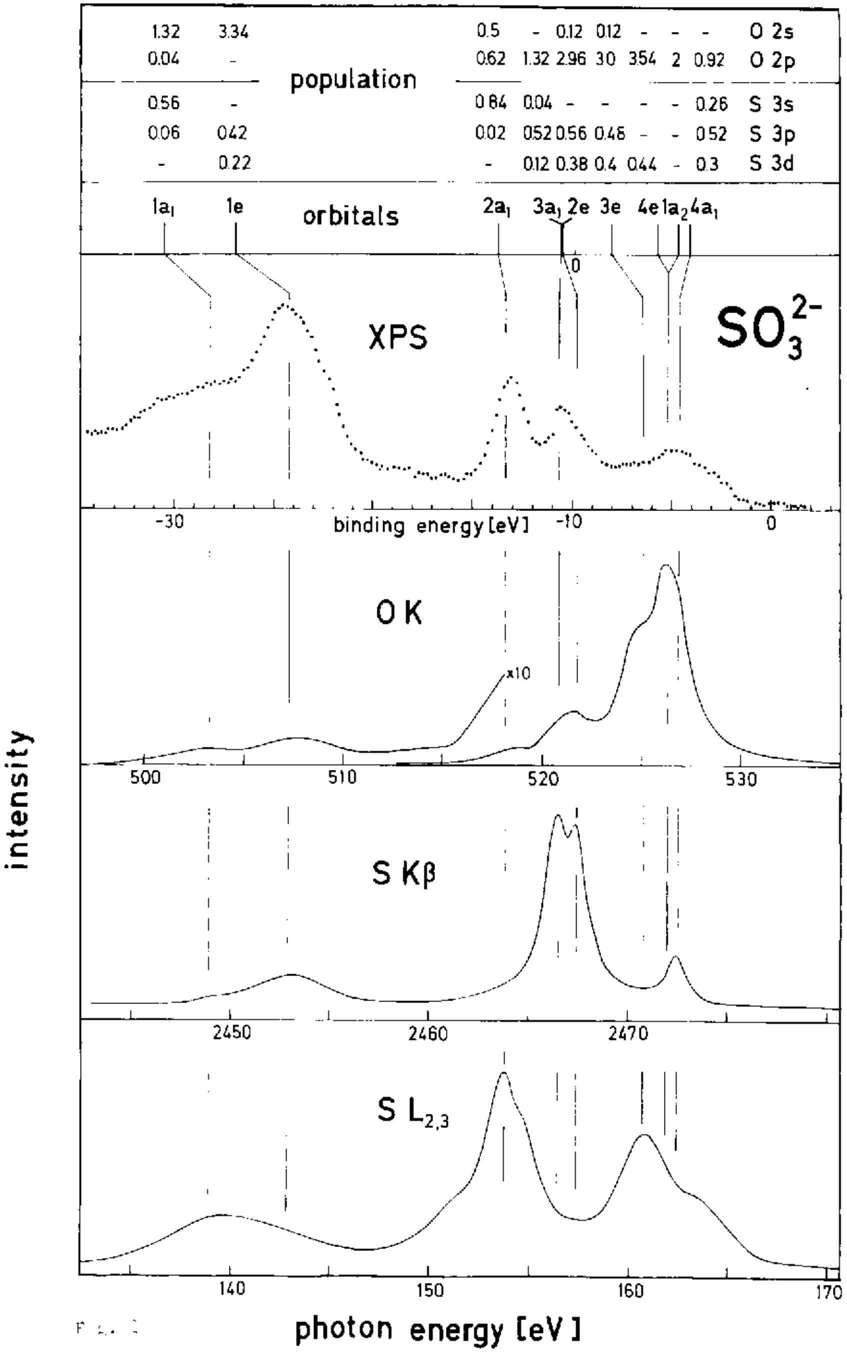
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0.06 0.42 0.02 0.52 0.56 0.48 - - 0.52 S 3p
- 0.22 - 0.12 0.38 0.4 0.44 - 0.3 S 3d
1a$_1$
1e
orbitals
2a$_1$
3a$_1$
2e
3e
4e
1a$_2$
4a$_1$
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SO$_3^{2-}$
XPS
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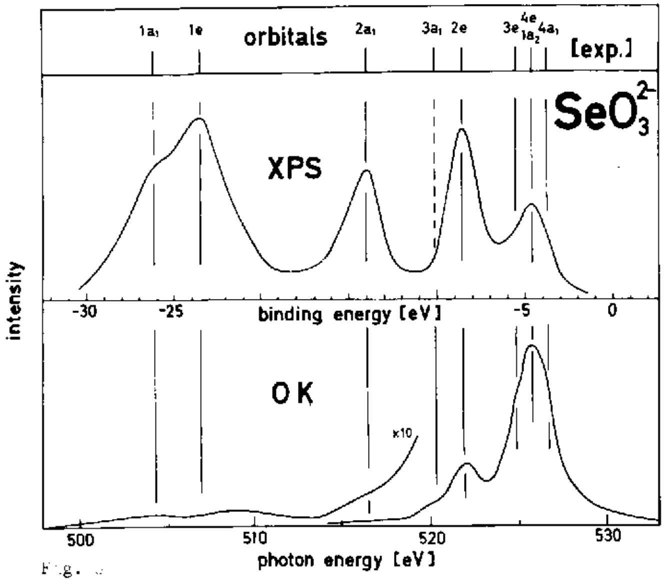

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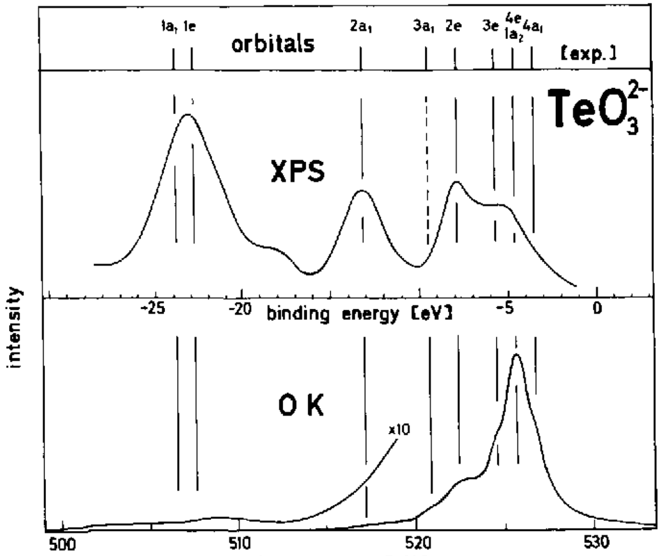
photon energy [eV]

Fig.



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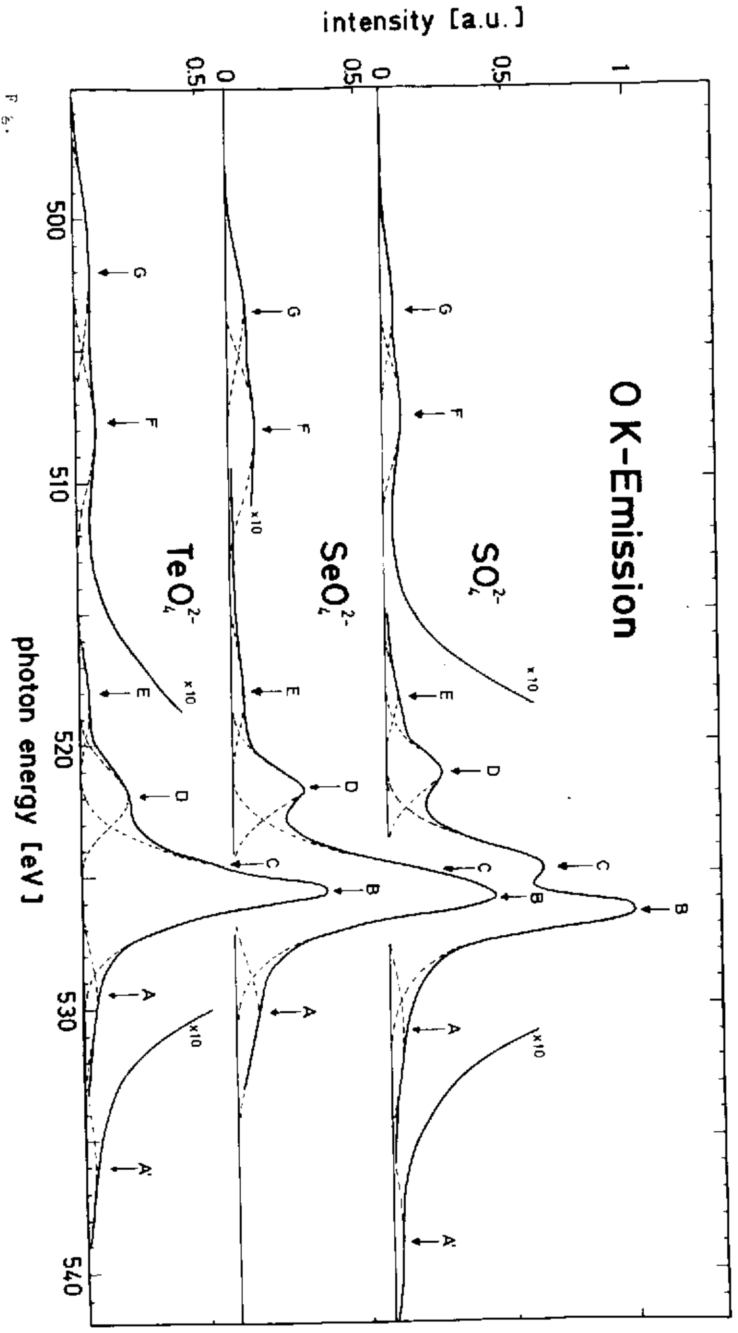
1a₂
4a₁
[exp.]
TeO₃²⁻
XPS
intensity
-25
-20
binding energy [eV]
-5
0
O K
x10
500
510
520
530
photon energy [eV]

Fig. 4



intensity [a.u.]
0.5
0
0.5
0
0.5
1
O K-Emission
SO₄²⁻
SeO₄²⁻
TeO₄²⁻
x10
G
F
E
D
C
B
A
A'
500
510
520
530
540
photon energy [eV]

Fig.

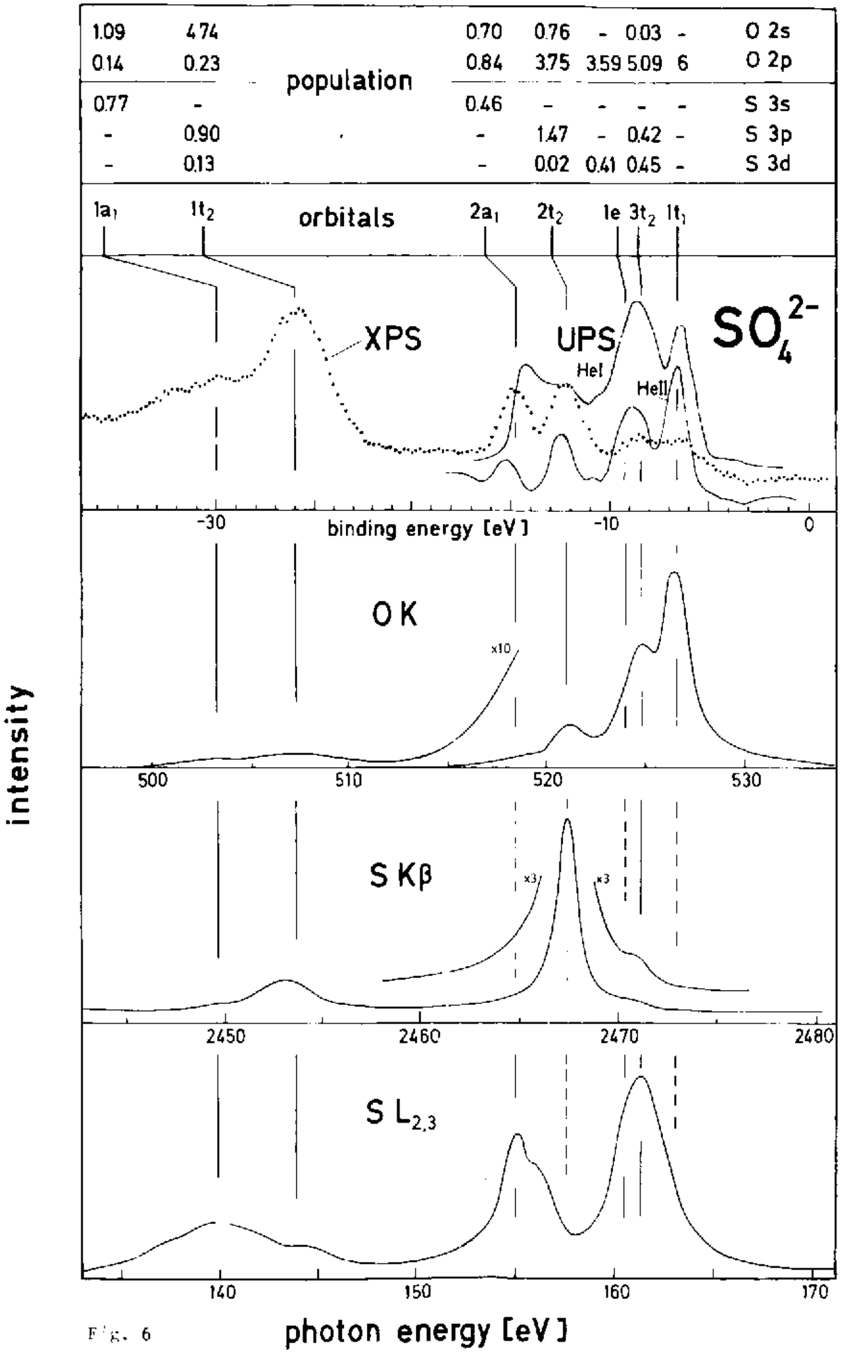

1.09 4.74 0.70 0.76 - 0.03 - O 2s
0.14 0.23 0.84 3.75 3.59 5.09 6 O 2p
population
0.77 - 0.46 - - - - S 3s
- 0.90 - 1.47 - 0.42 - S 3p
- 0.13 - 0.02 0.41 0.45 - S 3d
1a₁
1t₂
orbitals
2a₁
2t₂
1e
3t₂
1t₁
XPS
UPS
HeI
HeII
SO_4^{2-}
-30
binding energy [eV]
-10
0
O K
x10
500
510
520
530
S Kβ
x3
x3
2450
2460
2470
2480
S $L_{2,3}$
140
150
160
170
intensity
photon energy [eV]

Fig. 6

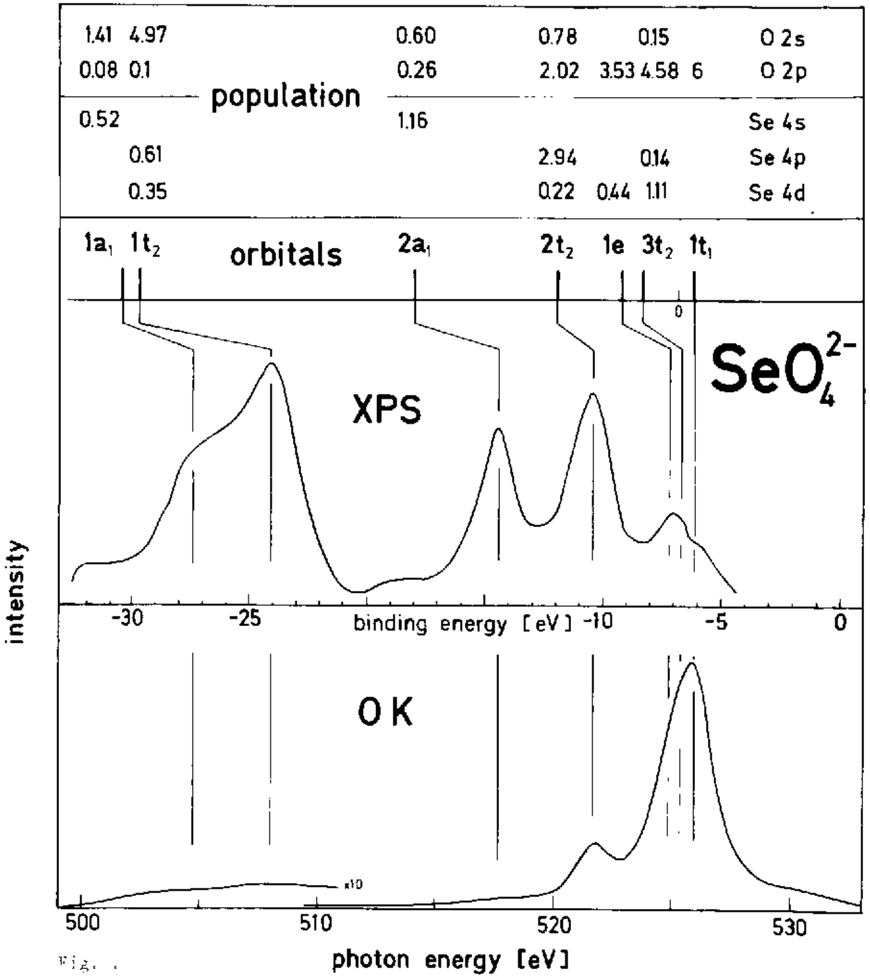

1.41 4.97 0.60 0.78 0.15 O 2s
0.08 0.1 0.26 2.02 3.53 4.58 6 O 2p
population
0.52 1.16 Se 4s
0.61 2.94 0.14 Se 4p
0.35 0.22 0.44 1.11 Se 4d
1a₁
1t₂
orbitals
2a₁
2t₂
1e
3t₂
1t₁
0
XPS
SeO_4^{2-}
-30
-25
binding energy [eV]
-10
-5
0
O K
x10
500
510
520
530
intensity
photon energy [eV]

Fig. .