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X-ray Spectroscopic Studies of the Electronic Structure of the Oxyanion PO_4^{3-}

by

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The oxygen K-emission spectrum of the lithium salt of PO_4^{3-} *excited in fluorescence using the synchrotron radiation of the storage ring DORIS in Hamburg was measured. With the aid of available X-ray* $P\ K\beta$*- and* $P\ L_{2,3}$*-emission spectra, X-ray photoelectron spectra, and MO-calculations, a consistent description of the electronic structure of the oxyanion* PO_4^{3-} *can be obtained.*

Introduction

In X-ray spectroscopic investigations of the electronic structure of chemical compounds one often encounters the difficulty that the samples are decomposed under electron bombardment. For this reason fluorescence excitation is frequently used in the region of soft X-rays. However, in the region of ultrasoft X-rays ($\lambda > 20$ Å), it is difficult to obtain spectra of sufficient intensity with fluorescence excitation if conventional X-ray tubes are used.

Attempts to use synchrotron radiation as a light source for the excitation of ultra-soft X-ray spectra of substances which cannot be investigated with primary excitation have been successful [1-3]. Recently the O K-spectrum of a number of oxyanions, the electron structure of which has of late found great interest, was studied using this kind of excitation. In this paper a report on the O K-spectrum of the phosphate anion PO_4^{3-} is given. The X-ray spectra of the central P-atom of this ion are known, and these, together with the O K-spectrum, are compared with X-ray photoelectron spectra (XPS) and discussed with regard to MO-calculations of PO_4^{3-}.

Experiment

The synchrotron radiation of the storage ring DORIS of the Deutsches Elektronen-Synchrotron DESY in Hamburg was used for the excitation of the oxygen spectrum. The characteristic radiation of the sample was taken off at an angle of about 9° and analysed in a 2 m concave grating spectrometer with an open parallel plate multiplier. A grating with 2400 lines/mm was used. The resolution was 0.5 eV.

The construction of the spectrometer allows the dispersion curve to be determined precisely. The energy calibration of the spectrometer was performed by means of the O K-spectrum of crystalline SiO_2, using the value for the energy of the main peak determined by Klein and Chun (4).

The samples of powdered Li_3PO_4 were rubbed onto a scratched aluminum plate. Li_3PO_4 was chosen because this salt has a low self-absorption for the oxygen radiation. The spectrum was measured stepwise at intervals of 0.1 eV.

The O K-spectrum

Measurements of the O K-spectrum of an oxyanion in different salts showed that the cation is without influence within the accuracy of the measurements. This is in agreement with observations of Prins (5) who found only small differences in the photoelectron spectra of different sulphates. The same author also showed that the hole in the K-shell of an oxygen atom is without significant influence upon the electronic structure of an oxyanion. We therefore compare in the following the observed O K-spectrum with the XP-spectrum and the P X-ray spectra of PO_4^{3-} and discuss these spectra in relation to MO-calculations of the free PO_4^{3-}-ion with T_d-symmetry.

The O K-spectrum of PO_4^{3-} is presented in Fig. 1. In the region of 515-530 eV, the spectrum is characterised by a pronounced maximum at 526.0 eV and additional structural features of decreasing intensity on its low-energy side. Between 500 and 510 eV structures of very low intensity were found; the resolution in this case was only 2 eV.

The spectrum can be separated into six symmetrical lines, A, ..., F. The limits of error given in Fig. 1 relate to the precision of the energy values relative to that of the most intense line A. The ratio of the integral intensities of the lines is 100:24:11:2:1:1, the error of the intensity values of the lines A, B, and C being within ± 20 %, that of the lines D, E, F being within ± 50 %.

The X-ray Spectra of the Central P-Atom

The O K-spectrum yields information only about the valence orbitals containing O 2p-electrons. Information about the P 3p-, and the P 3s- and P 3d-components of the molecular orbitals is obtained from the P Kβ-emission spectrum and the P $L_{2,3}$-emission spectrum, respectively.

The P Kβ-spectrum of phosphates was measured by Fichter (6) and Dolenko et al. (7). For the following discussion the spectrum of Na_3PO_4 obtained by Fichter with fluorescence excitation is used. The spectra of other ionic phosphates are very similar to each other (6), so one may rightly assume that the P Kβ-spectrum obtained with Na_3PO_4 is practically identical with that one would obtain with Li_3PO_4.

The P $L_{2,3}$-spectrum of the phosphates Na_3PO_4 and $AlPO_4$ was measured by Wiech (8) and that of KH_2PO_4 by Nefedov et al. (9). The spectra were excited by electron impact, hence one has to take into account that the spectra might be disturbed by partial decomposition of the samples, which indeed was observed in the case of Na_3PO_4, but not for $AlPO_4$. So the P $L_{2,3}$-spectrum of $AlPO_4$ is used in the following discussion.

Assignment of the X-ray Spectra and Comparison with XPS-Measurements

The X-ray spectra of oxygen and phosphorus in the PO_4^{3-}-ion are shown in Fig. 2, together with an X-ray photoelectron spectrum of PO_4^{3-} obtained with a sample of Li_3PO_4. Several authors have measured this spectrum (5,10,11), the one shown in Fig. 2 is the spectrum measured by Nefedov et al. (11).

The energy scales of the X-ray spectra and the photoelectron spectrum can be unambiguously aligned to each other in the following way. P Kβ and P $L_{2,3}$ can be related using the P $K\alpha_{1,2}$ energy (6). An alignment of the X-ray spectra to the XP-spectrum is possible by means of the binding energies for P 2p and O 1s which were measured by Connor et al. (10) and Nefedov et al. (11), respectively. Since the XPS-measurements of PO_4^{3-} of these authors are in good agreement, an unambiguous alignment of all spectra is obtained.

When the spectra were aligned to each other in the manner discussed above, corresponding structural features showed deviations of their energy position of some tenths of an electronvolt, which may result from differences of the energy calibration and the positioning of the maxima. By a slight shifting of the spectra (between 0.1 and 0.5 eV) the alignment was greatly improved. The final alignment of all the spectra is shown in Fig. 2. Corresponding structural features are indicated by vertical lines.

Comparison with MO-Calculations

In recent years several authors have calculated the electronic structure of the oxyanion PO_4^{3-} (10,12-15). The order of the molecular orbitals on an energy scale turns out to be the same in all calculations, however, there are differences in the actual orbital energies and in the population of the orbitals. Of the theoretical results those of Johansen (13) come closest to the experimental data.

For the assignment of the molecular orbitals and the experimental data, the results of the MO-calculation of Johansen were used. The relative orbital energies and the population analysis of orbitals are shown in the uppermost part of Fig. 2.

There are seven occupied orbitals of different binding energy, two orbitals with higher energy, $1a_1$ and $1t_2$, and five orbitals of lower binding energy, $2a_1$, ..., $1t_1$. These two groups of orbitals are clearly reflected in the spectra.

The assignment of the orbitals and the structures of the X-ray spectra can be made using the orbital population and the observed intensities of the structural features, taking into account the dipole selection rules.

The PO_4^{3-}-ion has T_d-symmetry. Hence transitions into the P K-level are allowed only from t_2-orbitals. Obviously the $2t_2$-orbital, having a high P 3p-component, has to be assigned to the main maximum of the P Kβ-spectrum. The comparatively high O 2p-component of this orbital gives rise to the lower maximum of the O K-spectrum at 521.6 eV.

The weak structure in the O K-spectrum at 519.3 eV corresponds to transitions from the $2a_1$-orbital which has a low O 2p-component. The peak of the P $L_{2,3}$-spectrum at 120.0 eV has to be assigned to the same orbital with its comparatively high P 3s-population.

The orbitals $1a_1$ and $1t_2$ correspond to the structures between 500 and 510 eV in the O K-spectrum and the two maxima of low intensity in the P Kβ- and P $L_{2,3}$-spectrum. The calculated binding energy of these two orbitals appears to be too high (10,12-14) or too low (15). - The high O 2s-population and the large cross-section of these s- electrons for X-rays is responsible for the pronounced maximum in the XP-spectrum. The extremely low intensity of the structures of the O K-spectrum in the 500 to 510 eV range is in agreement with the very low O 2p-population of the orbitals $1a_1$ and $1t_2$.

The assignment of orbitals 1e, $3t_2$ and $1t_1$ is beset with some difficulties. According to Nefedov et al. (11) the maximum in the XP-spectrum at a binding energy of about -11.5 eV corresponds to the 1e-and the $3t_2$-orbital, and the maximum near -10.5 eV to the $1t_1$-orbital. This interpretation is not in agreement with the X-ray spectroscopic observation: the line A in the O K-spectrum is found to be more intense than the line B. The total of the spectroscopic data rather shows that the two orbitals $3t_2$ and $1t_1$ are close together and have to be assigned to the maximum at −10.5 eV of the XP-spectrum and to the main line A of the O K-spectrum, whereas the line B of the O K-spectrum corresponds to the 1e-orbital. With this assignment the intensity ratio of A and B is roughly in agreement with the O 2p populations of the corresponding orbitals, $3t_2/1t_1$ and 1e. Finally the main maximum of P $L_{2,3}$ corresponds to transitions of the P 3d electrons of the orbitals 1e and $3t_2$.

The P 3p-component of the $3t_2$-orbital is reflected by the structure about 3.5 eV above the main maximum of P $K\beta$, as observed by Dolenko et al. (7) and also indicated in Fichter's curve; this structure, however, is of very low intensity indicating that the population of $3t_2$ is smaller than Johansen's value of 0.45 but not zero as calculated by Connor et al. (10).

In conclusion, it is found that the experimental observations confirm the order of the calculated orbitals. As to the energy values of the orbitals, there are some discrepancies as particularly with the energies of the $1a_1$- and $1t_2$-orbitals. According to Connor et al. this is due to the fact that the greater relaxation energy together with the ionization from this lower valence orbital leads to a greater error in using Koopman's theorem. In addition the distance of the orbitals $3t_2$ and $1t_1$ seems to be smaller than calculated as shown above.

As to the atomic orbital composition and the orbital populations, there is satisfactory correspondence between the theoretical values and the X-ray spectra including the relative intensities of their structures.

The consistency of the results seems to show that a comparison of the O K-spectrum with the other spectra of PO_4^{3-} and the interpretation of the spectra in terms of MO-calculations of the free PO_4^{3-}-ion is justified.

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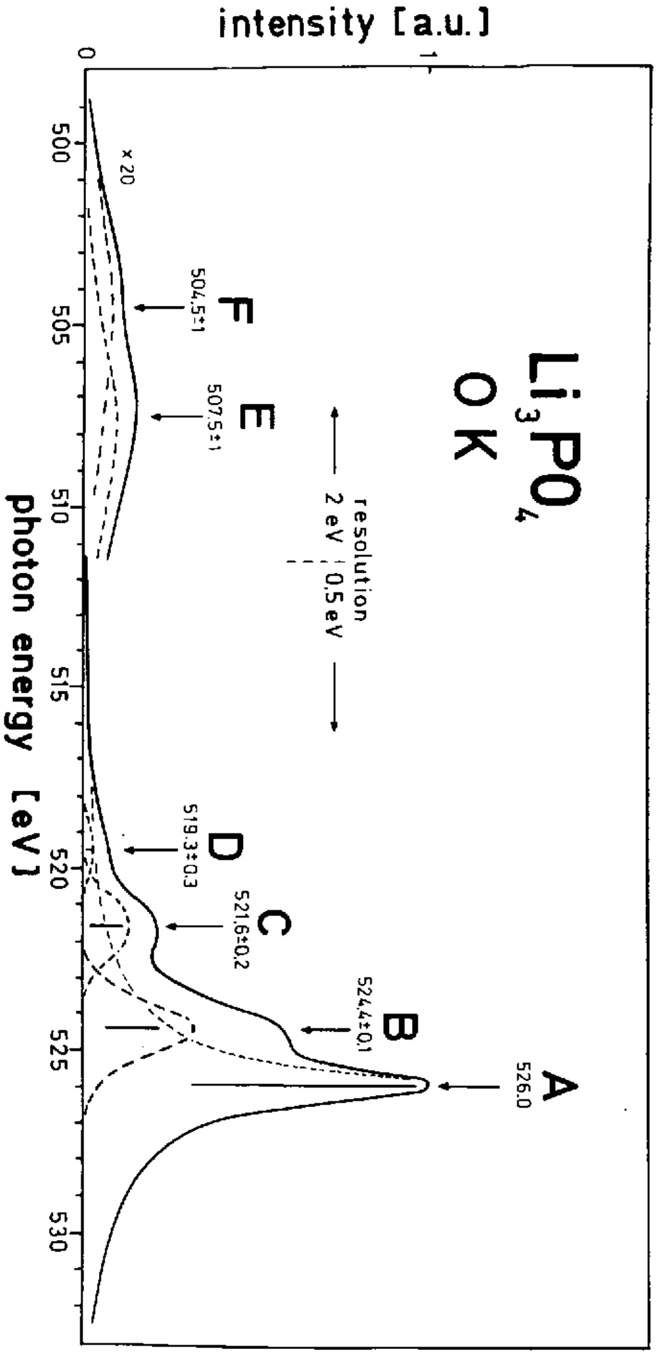
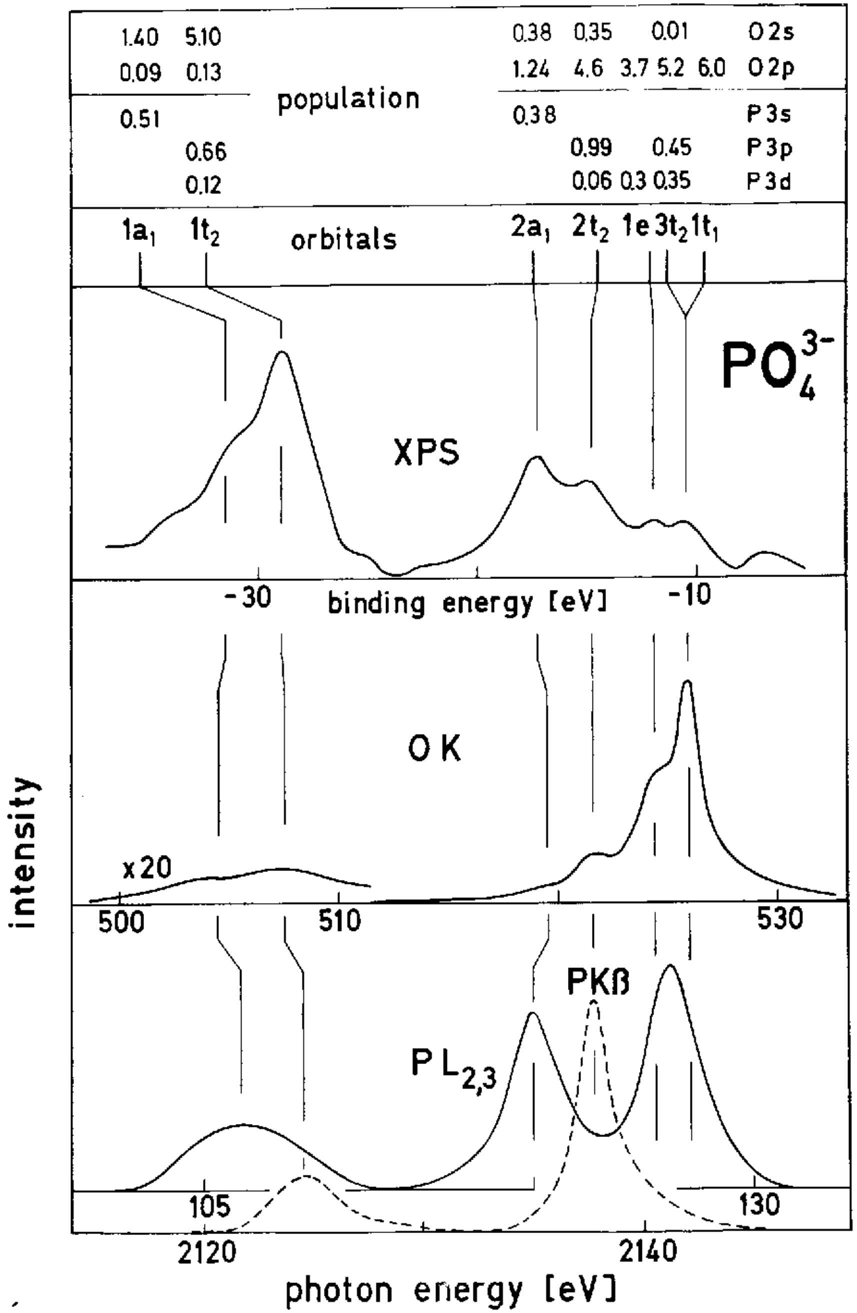
Figure captions

Fig. 1: O K-emission spectrum of Li_3PO_4 and its deconvolution into symmetrical lines

Fig. 2: O K-emission spectrum of PO_4^{3-}, together with P Kβ-emission spectrum (6), P $L_{2,3}$-emission spectrum (8), X-ray photoelectron spectrum (10), and electronic structure (13)


Li$_3$PO$_4$
O K
intensity [a.u.]
0
1
photon energy [eV]
500
505
510
515
520
525
530
x 20
F 504.5±1
E 507.5±1
D 519.3±0.3
C 521.6±0.2
B 524.4±0.1
A 526.0
resolution
2 eV
0.5 eV


PO$_4^{3-}$
population
1.40 5.10
0.09 0.13
0.51
0.66
0.12
0.38 0.35 0.01 O 2s
1.24 4.6 3.7 5.2 6.0 O 2p
0.38 P 3s
0.99 0.45 P 3p
0.06 0.3 0.35 P 3d
orbitals
1a$_1$ 1t$_2$ 2a$_1$ 2t$_2$ 1e 3t$_2$ 1t$_1$
XPS
binding energy [eV]
-30
-10
O K
x 20
500
510
530
intensity
PKß
P L$_{2,3}$
105
130
2120
2140
photon energy [eV]