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Molecular Orbital Analysis of the CO_3^{2-} Ion by Studies of the Anisotropic X-Ray Emission of its Components

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Abstract

The K X-ray emission spectra of carbon and oxygen in calcite single crystals $CaCO_3$ were measured. Due to the polarization of the radiation the shape of both spectra shows a pronounced angular dependence, which makes it possible to separate the contributions of the π- and σ-valence electrons of the CO_3^{2-} ion to the X-ray spectra, and to determine the sequence and the binding energies of the valence orbitals.

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1. Introduction

In a recent paper we have studied the electronic structure of the oxyanion CO_3^{2-} with the help of the X-ray K-emission spectra of carbon and oxygen, and of available X-ray photoelectron spectra (1). It was possible to interpret the spectroscopic data on the basis of molecular orbital calculations in a satisfactory manner. The structural features of the spectra allow to determine the binding energies of the orbitals; the intensities of the components of the X-ray spectra yield information about the contributions of the atomic components to the different atomic orbitals.

In two cases, however, orbitals lying close together could not be separated due to the limited resolution of the spectrometer. Thus for the binding energies and the observed relative intensities of these orbitals only mean values were obtained.

In the present paper we demonstrate how the anisotropic emission of the characteristic X-radiation can be used to separate and to identify orbitals of different symmetry and to determine their energetic spacings.

It has been pointed out in several papers (2-4) that, for ionic crystals, the influence of the crystal environment on the electronic structure of complex ions can often be neglected. Therefore MO-calculations for the isolated ions can be used for the interpretation of X-ray spectra and photoelectron spectra.

Calculations of the molecular orbitals of the CO_3^{2-} ion have been carried out by several authors (5-7). There are 8 occupied valence orbitals for the oxyanion CO_3^{2-}: $3a_1'$, $2e'$, $4a_1'$, $1a_2''$, $3e'$, $4e'$, $1e''$ and $1a_2'$; for the energies see Fig. 1. The orbitals $1a_2''$ and $1e''$ are π-orbitals, the others are σ-orbitals. Between the various calculations considerable discrepancies do exist concerning the spacing and sequence of the orbitals. The measurement of angular dependent X-ray emission of single crystals provides a possibility to distinguish between the different theoretical results.

According to the dipole selection rules X-ray transitions of electrons from all orbitals into the O 1s level are allowed, but transitions into the C 1s level are allowed only from the orbitals e' and a_2''. For σ→1s transitions the radiation is polarized parallel to the planes of the CO_3^{2-} ion, for π→1s transitions it is polarized perpendicular to this plane. Accordingly in single crystals the shape of the spectrum is angular dependent. If the molecules or ions all are parallel to each other, the spectrum can be separated into its π- and σ-components in the same way as has already been shown for the K X-ray spectra of the layer crystals graphite (8,9) and hexagonal boron nitride BN (9, 10). The procedure of using angular dependence of intensity to separate π- and σ-contributions to the spectra, has been treated in detail in a previous paper (10).

2. Experimental

In calcite ($CaCO_3$, space group D_{3d}^6) the planar CO_3^{2-} ions are situated in planes which are parallel to each other and perpendicular to the principal axis of the crystal. These planes are at angles of 44,6° with the cleavage surface of the crystal. To measure the radiation parallel (perpendicular) to the layers it is therefore necessary that the radiation is taken off from the monocrystalline sample perpendicular (parallel) to the principal axis and this means at an angle of 44.6° (45.4°) to the cleavage surface.

It should be mentioned that the fact that the layers are at a particular angle to the cleavage surface allows us to use take-off angles of 0° and 90° with respect to the CO_3^{2-} layers. In the case of layer crystals like graphite it is practically impossible to use a take-off angle of 0°.

The spectra were excited using the synchrotron radiation of the storage ring DORIS and measured with the 2m concave grating spectrometer described in (11). The resolution was about 0.7 eV. The second order O K-spectrum which is superimposed to the low energy part of the C K-spectrum was substracted graphically.

3. Results and Discussion

The O K- and C K-emission spectra measured parallel and perpendicular to the CO_3^{2-} planes are shown in Fig. 1. The dotted curves show the

results for observation parallel to the CO_3^{2-} plane (original measurement); the full curves are the results for observation perpendicular to the CO_3^{2-} plane (smoothed out for reasons of clearance). In both curves the background is subtracted. The spectra measured for both orientations of the crystal were fitted in the low energy region, where only σ-electrons contribute to the intensity, and no changes in the shape of the spectrum due to anisotropic emission are to be expected.

The emission spectra observed perpendicular to the planes of the ions contain only σ-contributions, the spectra observed parallel to these planes reflect a maximum of π-contribution. The difference between the dotted curves ($\pi+\sigma$) and the full curves (only σ) thus gives a curve which represents the contribution of the π-electrons (dashed curves).

In Fig. 1 the resultant π-curve is higher by a factor of two compared with the curve for a polycrystalline sample with an isotropic distribution of the crystallites (10). By adding the curves for the π- and the σ-contributions and taking account of this factor two, curves are obtained for both carbon and oxygen which are in good agreement with the spectra obtained for carbon and oxygen with polycrystalline samples of Li_2CO_3 (1). In addition, the consistency of the present separation of the spectra is confirmed by measurements carried out at different intermediate take-off angles.

Fig. 2 shows the π and σ X-ray bands (their intensities corresponding to a polycrystalline sample) together with available photoelectron

spectra (12, 13) as well as calculations of the binding energies of the orbitals and their composition. The alignment of the spectra has already been discussed in our previous paper (1).

Since only the orbitals $1a_2''$ and $1e''$ of CO_3^{2-} have π-character, the features in the X-ray π-bands of oxygen and carbon can be attributed to these orbitals. Likewise the features of the X-ray σ-bands can be attributed in an unambiguous way to the σ-orbitals. By separating the measured X-ray spectra into π- and σ-bands the controversial sequence of the orbitals $3e'$ and $1a_2''$ (see top of Fig. 2) has been cleared up: the orbital $1a_2''$ is more weakly bound than the orbital $3e'$.

The binding energies as determined from the experimental data are listed in Table 1. The zero-mark of the energy scale was taken from the X-ray photoelectron measurements of Calabrese and Hayes (12) who used for calibration the 1s line of the vacuum contaminant carbon assumed to have a binding energy of 285.0 eV. As can be seen by studies of the anisotropic emission, a separation of orbitals with an energetic spacing of 0.4 eV is possible, though the instrumental resolution is only 0.7 eV.

It is expected that the UP spectra should reflect predominantly the 2p electrons of the valence orbitals (as do the O K- and C K-spectra). Therefore for the uppermost orbitals $4e'$, $1e''$ and $1a_2'$ a similar shape for the O K-emission and the UP spectrum is expected. Experimentally it is found that the orbital $1a_2'$ in the X-ray spectrum is

more pronounced than the UP spectrum. This means that for this orbital the transition probability for O K-emission is rather large indicating that this orbital is localized at the oxygen atoms and therefore is almost wholly non-bonding in character.

In the X-ray spectra the intensity of the π-bands is lower than expected from the calculated populations. Thus, according to the calculations the C 2p component is 0.8 for the orbital $1a_2''$ as well as for the orbital 3e', while the observed intensity ratio σ:π is near 2:1. Similarly the contribution of the O π-band to the main maximum of the O K-spectrum is lower than expected from the population of the 1e" orbital.

A similar effect was observed for the X-ray emission spectra of hexagonal boron nitride (14), and benzene and naphthalene (15). It therefore seems that the intensities of X-ray spectra cannot be explained quantitatively on the basis of the population data of the valence orbitals; in addition the overlap of the different orbitals should be considered.

Acknowledgements

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Table 1: Binding energies of the valence orbitals of the CO_3^{2-} ion

Orbital	Binding energy (in eV)
$1a_2'$	-4.7 ± 0.2
$1e''$	-5.2 ± 0.2
$4e'$	-6.2 ± 0.2
$1a_2''$	-9.6 ± 0.2
$3e'$	-10.0 ± 0.2
$4a_1'$	-12.0 ± 0.2
$2e'$	-24.0 ± 1.0
$3a_1'$	-26.6 ± 1.0

Figure Captions

Fig. 1: O K- and C K-emission spectrum of calcite single crystals, parallel (dotted) and perpendicular (full line) to the plane of the CO_3^{2-} ion. The dashed line shows the π-part of the emission parallel to the plane of the ion.

Fig. 2: π- and σ-parts of the oxygen and carbon spectrum of CO_3^{2-}, together with UPS and XPS measurements (12, 13) and calculated electronic structure (6,7).

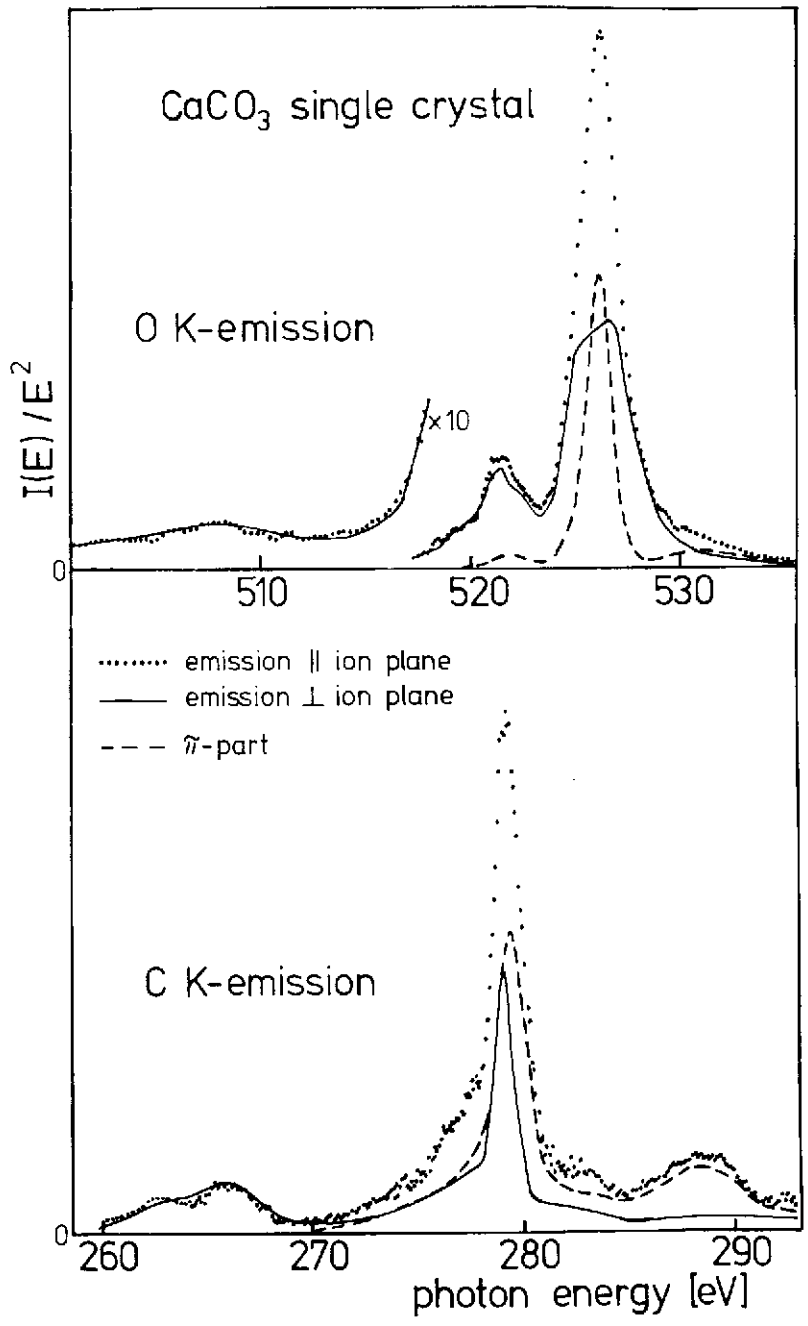
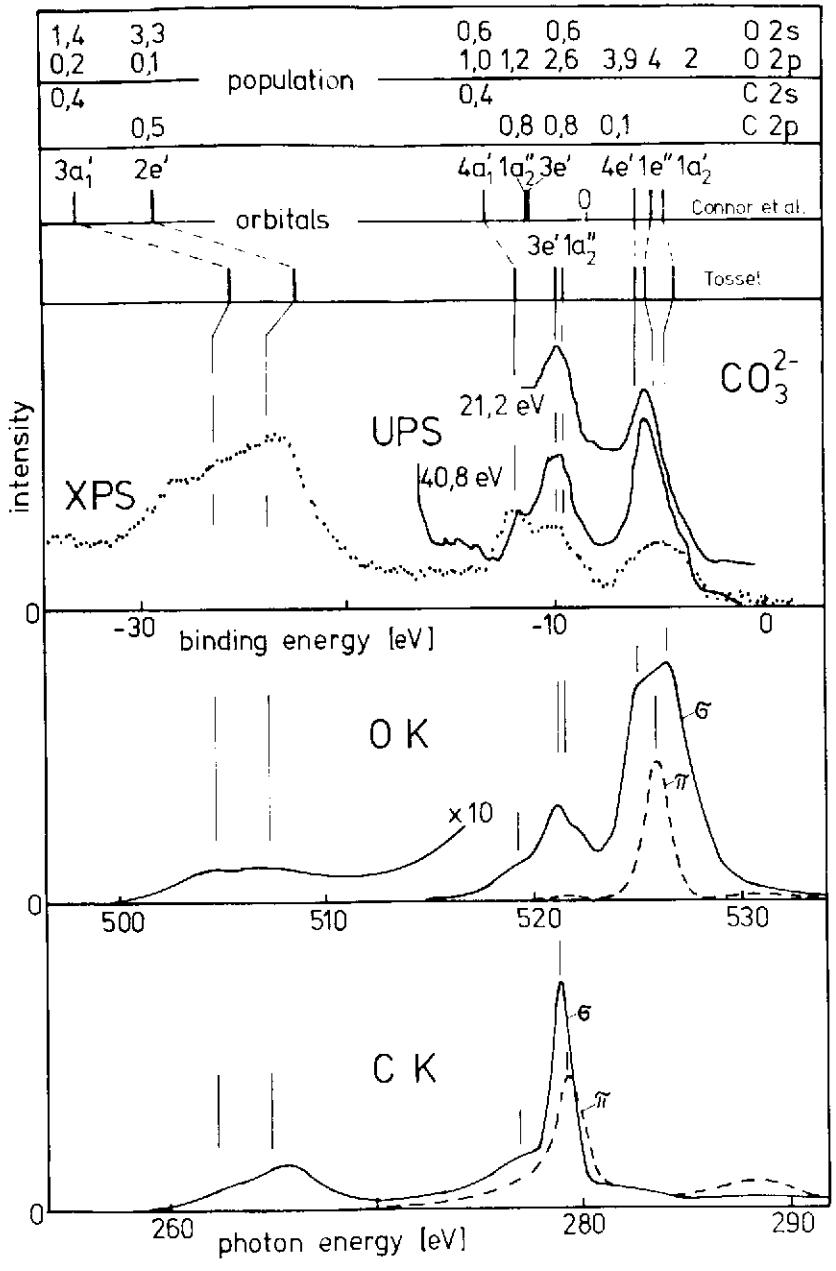


Fig. 1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O 2p
C 2s
C 2p
3a1' 2e'
orbitals
4a1' 1a2" 3e' 4e' 1e" 1a2'
0
Connor et al.
3e' 1a2"
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CO3 2-
21,2 eV
UPS
40,8 eV
XPS
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-30
binding energy [eV]
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500
510
520
530
C K
σ
π
0
260
photon energy [eV]
280
290