

DESY SR-77/14  
August 1977

DESY-Bibliothek  
29. AUG. 1977

X-Ray Spectroscopic Studies of the Electronic Structure of the  
Oxyanions  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{CO}_3^{2-}$

by

N. Kosuch, E. Tegeler, G. Wiech and A. Faessler  
*Sektion Physik der Universität München*

To be sure that your preprints are promptly included in the  
HIGH ENERGY PHYSICS INDEX ,  
send them to the following address ( if possible by air mail ) :

DESY  
Bibliothek  
Notkestraße 85  
2 Hamburg 52  
Germany

X-ray Spectroscopic Studies of the Electronic Structure of the  
Oxanions  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{CO}_3^{2-}$

N. Kosuch, E. Tegeler, G. Wiech and A. Faessler

Sektion Physik der Universität München, 8000 München 22, West Germany

Abstract

Using synchrotron radiation for excitation, the K-emission spectra of nitrogen and oxygen in  $\text{NO}_2^-$  and  $\text{NO}_3^-$  and of carbon and oxygen in  $\text{CO}_3^{2-}$  were measured. The x-ray spectra together with available photoelectron spectra permit a precise positioning of the occupied orbitals of the anions. The intensities of the x-ray spectra provide information on the atomic orbital composition. In general the agreement between the experimental results and those of MO-calculations is satisfactory; in some cases, however, there are considerable discrepancies.

1. Introduction

The electronic structure of oxanions has found considerable interest in recent years. Numerous oxanions have been studied by photoelectron spectroscopy and to some extent also by x-ray spectroscopy. In an x-ray spectroscopic study of the  $\text{PO}_4^{3-}$ -ion recently published (1) it could be shown, that the x-ray emission spectra of both atoms of an oxanion in combination with photoelectron spectra and MO-calculations allow a consistent description of the electronic structure of the occupied states of the ion.

The present paper is a report on the x-ray K-emission spectra of nitrogen and oxygen in  $\text{NO}_2^-$  and  $\text{NO}_3^-$  and of carbon and oxygen in  $\text{CO}_3^{2-}$ . On account of the dipole selection rules the K-emission spectra reflect atomic components with p-like symmetry. The x-ray photoelectron spectra (XPS) generally reflect all orbitals. Since for light elements the cross section ratio  $\sigma_s/\sigma_p \gg 1$ , for the oxanions in question orbitals with components of s-like symmetry contribute most strongly to the photoelectron spectra. So in the present study x-ray spectra and photoelectron spectra complement each other.

The x-ray spectra together with the photoelectron spectra allow a more precise determination of the positioning and of the binding energies of the orbitals. Information on the atomic orbital composition is obtained from the intensities observed in the x-ray spectra. The results are compared with those of MO-calculations of the three oxanions.

2. Experiment

The spectra were observed in fluorescence using for excitation the synchrotron radiation of the storage ring DORIS at the Deutsches Elektronen-Synchrotron DESY in Hamburg. A 2 m concave grating spectrometer was used to disperse the radiation (2), and an open parallel plate multiplier served as detector (3). The instrument was calibrated with the help of the O K-spectrum of  $\text{SiO}_2$  (4), the dispersion curve of the instrument being known. The spectral resolution was about 0.6 eV, except for the observation of the very weak low-energy part of the oxygen K-spectrum where it was reduced to 2 eV.

The samples were prepared by rubbing powdered  $\text{NaNO}_2$ ,  $\text{LiNO}_3$ , and  $\text{Li}_2\text{CO}_3$  under dry argon gas onto scratched aluminium plates. The plates were mounted on a holder cooled with liquid nitrogen. The take-off angle was always  $9^\circ$ . At 2 GeV and 150 mA typical counting rates for the main peak of the spectra were about

$10^3$  c/min.

The pressure in the sample chamber was less than  $10^{-8}$  torr. Test measurements were made to make sure that the spectra were not disturbed by contamination of the samples. All compounds proved to be stable during the time of several runs. The time for one run varied between 0.5 and 2 hours.

### 3. Alignment of the x-ray and photoelectron spectra and comparison with MO-calculations

The x-ray spectra of oxygen and the central atoms of the three oxyanions extend over an energy range of about 30 eV. The main intensity is concentrated in a region of about 10 eV in the high energy part of the spectrum. The structures in the low energy part are very weak especially in the O K-spectrum.

In order to determine the positions and the intensities more precisely, the observed x-ray spectra were separated graphically into symmetrical components, as far as this was possible.

Some orbitals show up as features in the spectrum of both the central atom and the oxygen atom. Hence it is possible - by means of the spacing of these structural features - to align the two spectra so that features corresponding to a certain orbital appear below each other. The spectra thus aligned are shown for the three ions in Figs. 1-3. As can be seen, nearly all features in the oxygen spectrum correspond to a feature in the nitrogen or carbon spectrum, respectively. - The XP-spectrum can be aligned to the x-ray spectra in the same manner.

The positions of the occupied valence orbitals as determined by this alignment of the x-ray and photoelectron spectra are unambiguous; they are indicated in the figures by vertical lines. - Using the position of the vacuum level fixed by the XPS-measurements one obtains values of the binding energies of the orbitals which are more precise than those derived only from XPS-curves.

The orbitals found spectroscopically are then compared with the results of MO-calculations of the ion in question (inserted in the upper part of the figures). The assignment of the orbitals was carried out with the help of the calculated orbital energies and the population data. To correlate the energy scale of the calculated and that of the spectroscopically found orbitals the first one was shifted to adapt the orbitals with a high O 2p-component to the

main maximum of the O K-emission spectrum. It will be seen that the assignment can be carried out unambiguously.

The intensity distribution of the x-ray spectra provides information about the relative populations of the molecular orbitals. Since the number of transitions is approximately proportional to the population of an orbital with 2p-components (5), the relative intensity distributions in the K-spectra correspond approximately to the relative populations of the atomic p-components of the orbitals.

It should be stated here, that the hole in the K-shell of an oxygen atom has no measurable effect on the electronic structure of the oxyanion (6). Moreover the oxygen K-spectra of an oxyanion from different salts do not show an influence of the cation within the accuracy of the measurements (1).

### 4. Results

#### The $\text{NO}_2^-$ -Ion

The x-ray emission spectra of nitrogen and oxygen of the oxyanion  $\text{NO}_2^-$  have been measured for the first time. Two XPS-measurements have been reported (7)(8). The x-ray spectra obtained with a sample of  $\text{NaNO}_2$  together with the newest XPS-curve of  $\text{LiNO}_2$  of Calabrese and Hayes (7) are shown in Fig. 1.

The various MO-calculations of  $\text{NO}_2^-$  ( $C_{2v}$ -symmetry) do not show significant differences (9-13), the newest ones being practically identical. The results of the calculation of Pfeiffer and Allen (12) were used for a comparison with the spectroscopic data. In the upper part of Fig. 1 are inserted the calculated positions of the orbitals and the partial gross population (in electrons) of N 2s, N 2p, O 2s and O 2p. - As can be seen, all states found spectroscopically - with the exception of the low maximum at 381.7 eV in the N K-spectrum - correspond to orbitals obtained in the calculations.

The energy values of the structural features of the two x-ray spectra and the values of the binding energies of the orbitals are presented in Table 1. Obviously the x-ray spectra contribute considerably to a better determination of the binding energies for the different orbitals. It is true, the binding energies of the inner three valence orbitals are well defined by the XP-spectrum, but a more precise determination of the binding energies of the outer orbitals is only possible with the x-ray spectroscopic data.

The coordination of the XP- and K-spectra also allows one to determine the binding energies of the K-electrons of the two atoms. Using the zero-point of the XP-spectrum, one finds for the oxygen 1s electrons a binding energy of -531.1 eV and for the nitrogen 1s electron the value -402.8 eV. The latter binding energy has also been measured by Wyatt et al. (13) for  $\text{KNO}_2$ ; these authors obtained a value of -403.3 eV. The good agreement of the two values confirms the coordination of the XP- and K-spectrum.

The integral intensities of the x-ray features of both spectra in Table 1 are given in percents of the total intensity of the spectrum. The values in the next column give the calculated distribution of the O 2p and N 2p components in percents of all O 2p and N 2p components. A comparison of these values with the spectral intensity values shows that in a few cases there are considerable differences. Some of these are such that they cannot be explained by the inaccuracy of the graphical separation of the spectra in components. In the case of oxygen, the ratio of the calculated O 2p components of the orbital group ( $4b_2, 1a_2, 6a_1$ ) - corresponding to the main maximum of the spectrum - and of the orbital group ( $3b_2, 1b_1$ ) - corresponding to the lower maximum - is 2,5 : 1, while the measured intensity ratio is 7,5 : 1. A similar discrepancy is found for nitrogen. The main maximum of the nitrogen spectrum can be separated into two components with the intensity ratio of about 1,7 : 1, while the ratio of the calculated N 2p components of the corresponding orbitals  $5a_1$  and ( $3b_2, 1b_1$ ) is 0,5 : 1.

#### The $\text{NO}_3^-$ -ion

The x-ray spectrum of nitrogen in  $\text{NO}_3^-$  has not been measured so far. The x-ray K-spectrum of oxygen in this ion was observed by two authors (14)(15). However, it seemed desirable to remeasure the O K-spectrum under better experimental conditions. A sample of  $\text{LiNO}_3$  was used. For the same compound three XPS-curves have been published (7)(8)(16). The two x-ray spectra, together with the photoelectron spectrum measured by Calabrese and Hayes (7), are shown in Fig.2.

MO-calculations of the  $\text{NO}_3^-$ -ion ( $D_{3h}$ -symmetry) have been carried out by Wyatt et al. (13), and by Dolin et al. (17) with different methods. The somewhat different results are inserted in the upper part of Fig.2, including the population values calculated by the latter authors. All calculated orbitals are reflected in the spectra. However, there are features in all spectra at the high energy end which cannot be correlated with calculated orbitals. Another

feature in the spectra which cannot be interpreted is the asymmetry of the maxima corresponding to the  $2e'$  orbital.

The sequence of the orbitals as derived from the spectroscopic data is shown in Table 2. There is a discrepancy between the theoretical results of Wyatt et al. (13) and those of Dolin et al. (17) concerning the orbitals  $3e'$  and  $1a_2''$ . The XPS-data seem to confirm the sequence found by Wyatt et al., since only the  $3e'$  orbital has a component of s-symmetry which may be reflected by the maximum at a binding energy of about -11,8 eV. - The orbitals  $1e''$  and  $1a_2''$  have a separation of 0,13 eV according to the first authors and 1,4 eV according to the second authors. The intensity and shape of the main maximum of the O K-spectrum seem to be compatible only with the smaller value.

As in the case of  $\text{NO}_2^-$ , the binding energies of the outer orbitals of  $\text{NO}_3^-$  are better defined by the x-ray spectra, whereas those of the three inner valence-orbitals are better determined by the XP-spectra. - The binding energies of the K-electrons as obtained from the x-ray spectra are -532,5 eV for oxygen and -407,2 eV for nitrogen, relative to the zero-point of the XP-spectrum. These values are in good agreement with the mean values -533,0±0,2 eV for oxygen and -407,5±0,4 eV for nitrogen, calculated by Nejedov et al. (18) from the results of several investigations of  $\text{KNO}_3$ . This agreement confirms that the alignment of the three spectra is proper.

The calculated oxygen 2p components of the orbitals are reflected in the structural features of the x-ray spectrum with satisfactory agreement (Table 2). However, in the case of nitrogen, the intensity ratio of main maximum to lower maximum is about 10:1, whereas the ratio of the corresponding 2p components of orbital group ( $3e', 1a_2'', 4a_1'$ ) and orbital  $4e'$  is near 4:1.

#### The $\text{CO}_3^{2-}$ -ion

For the  $\text{CO}_3^{2-}$ -ion several XPS-measurements are available (7)(16)(19). The x-ray emission spectrum of oxygen published by Koster (14) shows fewer details than were expected, and therefore was remeasured. A sample of  $\text{Li}_2\text{CO}_3$  was used. The observed spectra are shown in Fig.3, together with the XP-spectrum of  $\text{Li}_2\text{CO}_3$  measured by Calabrese and Hayes (7).

MO-calculations for the  $\text{CO}_3^{2-}$ -ion ( $D_{3h}$ -symmetry) have been performed by several authors (17, 19, 20). Position and atomic composition of the orbitals inserted

in Fig.3 are calculated by Connor et al. (19). The distances of the orbitals calculated by Tossel (20) are also shown in Fig.3, because they agree very well - except for the somewhat too large spacing between  $1e''$  and  $1a_2'$  - with those found experimentally. According to both calculations the orbitals  $1a_2''$  and  $3e'$  are very close to each other, in agreement with shape and half-width of the main maximum of the C K-spectrum. The sequence of the two orbitals cannot be determined from the spectroscopic data. All calculated orbitals are reflected in the spectra, but there is structure in both spectra at the high energy end which cannot be correlated with a calculated orbital.

The energy values for the structural details of the x-ray spectra and the values for the binding energies are presented in Table 3. The binding energies are well defined, with the exception of those for the orbitals  $3a_1'$  and  $2e'$ , which are reflected in all three spectra by broad overlapping maxima.

The binding energy of the O 1s electrons relative to the zero-point of the XP-spectrum is found to be -531.2 eV. Nefedov et al. (16) measured -537.5 eV, using  $\text{Li}_2\text{CO}_3$ . This value is probably too high by about 5 eV, because these authors' values for the binding energies of the valence orbitals are also by about the same amount higher than those of the other authors (7, 19). - For C 1s the observed value is -288.8 eV.

For the intensities of the maxima of the oxygen K-spectrum and the 2p components of the corresponding orbitals ( $1a_1'$ ,  $1e''$ ),  $4e'$  and ( $3e'$ ,  $1a_2'$ ) similar discrepancies are found as in the case of  $\text{NO}_2^-$ . - The correspondence of the intensities of the main feature in the carbon spectrum and of the 2p components of the orbitals ( $3e'$ ,  $1a_2''$ ) and  $2e'$  is good.

It may be mentioned that, according to the selection rules, transitions from orbitals  $1a_2'$ ,  $1e''$ , and  $4a_1'$  to the K-level are forbidden, and in the MO-calculations the C 2p component of these orbitals is zero. However, in the C K-spectrum there is weak but distinct structure in positions corresponding to transitions from these orbitals. Such transitions indicate possibly that the  $D_{3h}$ -symmetry of the cation is disturbed.

Summarizing it may be stated that all essential features of the spectra can be correlated with the calculated orbitals. The sequence of the orbitals as determined from the x-ray spectra is the same as that of the calculated ones. In many cases the distances of the calculated orbitals are too large. - Generally the intensity distribution of the K-spectra reflects the population of the atomic 2p components satisfactorily; in some cases, however, there are considerable discrepancies. For a more quantitative comparison calculations of the intensity distribution of the x-ray spectra should be available.

#### Acknowledgements

This work was supported by the Deutsches Elektronen-Synchrotron DESY. Financial support by the Bundesministerium für Forschung und Technologie is gratefully acknowledged.

## Literature

- (1) N. Kosuch, E. Tegeler, G. Wiech and A. Faessler, Chem.Phys.Lett., 47 (1977) 96.
- (2) N. Kosuch, E. Tegeler, G. Wiech and A. Faessler, Nucl.Instr. and Meth., to be published.
- (3) W. Schnell and G. Wiech, Mikrochim. Acta, Suppl. 7 (1977) 323.
- (4) G. Klein and H.-U. Chun, phys.stat.sol., 49b (1972) 167.
- (5) G. Karlsson and R. Manne, Physica Scripta, 4 (1971) 119.
- (6) R. Prins, J.Chem.Phys. 61 (1974) 2580.
- (7) A. Calabrese and R.G. Hayes, J. Electron Spectrosc.Relat.Phenom., 6(1975)1.
- (8) M. Barber, J.A. Connor, I.H. Hillier and V.R. Saunders, in D.A. Shirley (Ed.), Electron Spectroscopy, North-Holland, Amsterdam, 1972, p. 379.
- (9) C. Petrongola, E. Scrocco and J. Tomasi, J. Chem. Phys., 48 (1968) 407.
- (10) R. Bonaccorsi, C. Petrongolo, E. Scrocco and J. Tomasi, J. Chem.Phys., 48 (1968) 1497.
- (11) H. Betsuyaku, J. Chem.Phys. 50 (1969) 3118.
- (12) G.V. Pfeiffer and L.C. Allen, J. Chem.Phys., 51 (1969) 190.
- (13) J.F. Wyatt, I.H. Hillier, V.R. Saunders, J.A. Connor and M. Barber, J. Chem.Phys. 54 (1971) 5311.
- (14) A.S. Koster, J. Phys.Chem.Sol., 32 (1971) 2685.
- (15) I.B. Borovskii, V.I. Matiskin and V.I. Nefedov, Journal de Physique, 32 (1971) C4-207.
- (16) V.I. Nefedov, N.P. Sergushin, I.M. Band und M.B. Trzhaskorskaya, J. Electron Spectrosc.Relat.Phenom., 2 (1973) 383.
- (17) S.P. Dolin and M.E. Dyatkina, J. Struct.Chem., 13 (1972) 906.
- (18) V.I. Nefedov, Ya.V. Salyn, G. Leonhardt and R. Scheibe, J. Electron Spectrosc.Relat.Phenom., 10 (1977) 121.
- (19) J.A. Connor, I.H. Hillier, V.R. Saunders and M. Barber, Mol.Phys., 23 (1972) 81.
- (20) J.A. Tossel, J. Phys.Chem.Sol., 37 (1976) 1043.

Tab. 1  $\text{NO}_2^-$ : molecular orbitals (MO), observed binding energies in eV (BE) energy values of corresponding features in the x-ray spectra in eV (Features), observed relative intensities in the x-ray spectra ( $I_{\text{exp}}$ ) and calculated relative atomic 2p-components (Theory)

M O	B E	Oxygen			Nitrogen		
		Features	$I_{\text{exp}}$	Theory	Features	$I_{\text{exp}}$	Theory
$6a_1$	$-3,2 \pm 0,2$	$528.2 \pm 0.3$	75	58,5	$399.8 \pm 0.2$	10	15,0
$1a_2$	$-4,6 \pm 0,1$	$526.7 \pm 0.1$			-	0	0
$4b_2$	$-5,6 \pm 0,2$	$524.8 \pm 0.2$			$397.4 \pm 0.3$	7	0,3
$1b_1$	$-8,5 \pm 0,3$	$522.7 \pm 0.3$	10	23,1	$394.5 \pm 0.3$	29	41,4
$3b_2$							
$5a_1$	$-10,0 \pm 0,3$	$521.1 \pm 0.5$	7	11,1	$392.9 \pm 0.3$	48	21,1
$4a_1$	$-13,6 \pm 0,2$	$518.5 \pm 1$	4	4,8	-	0	5,0
$2b_2$	$-25,3 \pm 1$	$506.5 \pm 1$	3	0,5	$377.6 \pm 0.6$	3	13,8
$3a_1$	$-30,5 \pm 1$	$501 \pm 1$	1	2,0	$372.4 \pm 0.5$	3	3,5

Tab. 2  $\text{NO}_3^-$ : molecular orbitals (MO), observed binding energies in eV (BE), energy values of corresponding features in the x-ray spectra in eV (Features), observed relative intensities in the x-ray spectra ( $I_{\text{exp}}$ ) and calculated relative atomic 2p-components (Theory)

M O	B E	Oxygen			Nitrogen		
		Features	$I_{\text{exp}}$	Theory	Features	$I_{\text{exp}}$	Theory
$1a'_2$	$-5.6 \pm 0.2$	$526.85 \pm 0.15$	75	74	-	0	0
$1e''$					-		
$4e'$	$-7.4 \pm 0.2$	$525.0 \pm 0.2$	14	21	$399.7 \pm 0.2$	8	14
$3e'$	$-11.8 \pm 0.2$	$521.9 \pm 0.15$			$395.3 \pm 0.3$	81	58
$1a''_2$	$-13.2 \pm 0.2$	-			$394.0 \pm 0.2$		
$4a'_1$	$-14.5 \pm 0.2$	$518.2 \pm 0.5$	4	1.6	$393.0 \pm 0.3$	11	28
$2e'$	$-26.2 \pm 0.8$	$506.7 \pm 0.8$	5	1.6	$381.1 \pm 0.8$		
$3a'_1$	$-31.7 \pm 0.8$	$501.2 \pm 0.8$	2	2.3	-		

Tab. 3  $\text{CO}_3^{2-}$ : molecular orbitals (MO), observed binding energies in eV (BE) energy values of corresponding features in the x-ray spectra in eV (Features), observed relative intensities in the x-ray spectra ( $I_{\text{exp}}$ ) and calculated relative atomic 2p-components (Theory)

M O	B E	Oxygen			Carbon		
		Features	$I_{\text{exp}}$	Theory	Features	$I_{\text{exp}}$	Theory
$1a'_2$	$-5.1 \pm 0.2$	$526.7 \pm 0.1$	80	66	$283.9 \pm 0.2$	4	0
$1e''$							
$4e'$	$-6.2 \pm 0.2$	$525.1 \pm 0.2$	13	25	$279.0 \pm 0.1$	0	4
$3e'$	$-9.9 \pm 0.2$	$521.4 \pm 0.2$				69	73
$1a''_2$	-	-					
$4a'_1$	$-12.1 \pm 0.2$	$519.1 \pm 0.3$	3	6.7	$276.6 \pm 0.4$	4	0
$2e'$	$-24.0 \pm 1$	$507.2 \pm 0.8$	2	0.7	$265.0 \pm 0.4$	23	23
$3a'_1$	$-26.6 \pm 1$	$504.5 \pm 0.5$	2	1.3	-	0	0



## Figure Captions

Fig. 1 : O K- and N K-emission spectrum of  $\text{NO}_2^-$  together with X-ray photoelectron spectrum (7), and calculated electronic structure (12).

Fig. 2 : O K- and N K-emission spectrum of  $\text{NO}_3^-$  together with X-ray photoelectron spectrum (7), and calculated electronic structure (13)(17).

Fig. 3 : O K- and C K-emission spectrum of  $\text{CO}_3^{2-}$  together with X-ray photoelectron spectrum (7), and calculated electronic structure (19)(20).

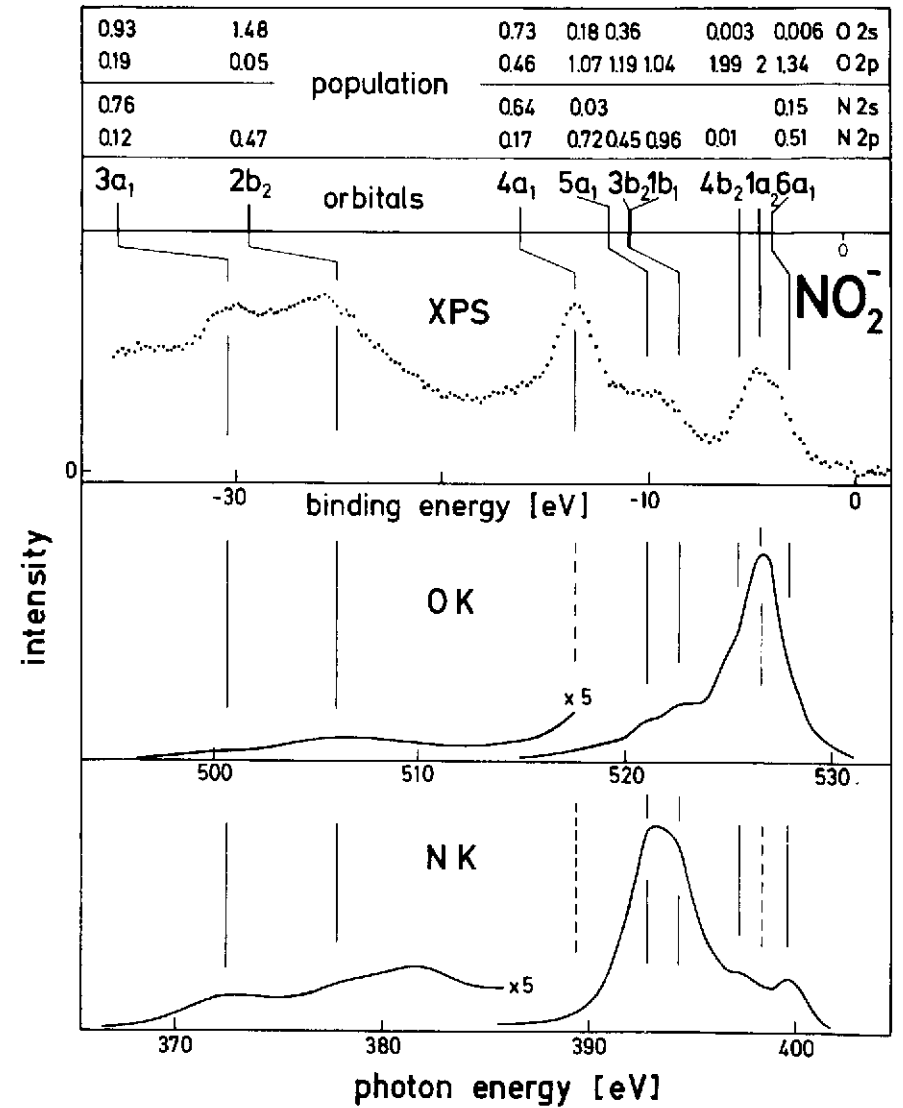


Fig. 1

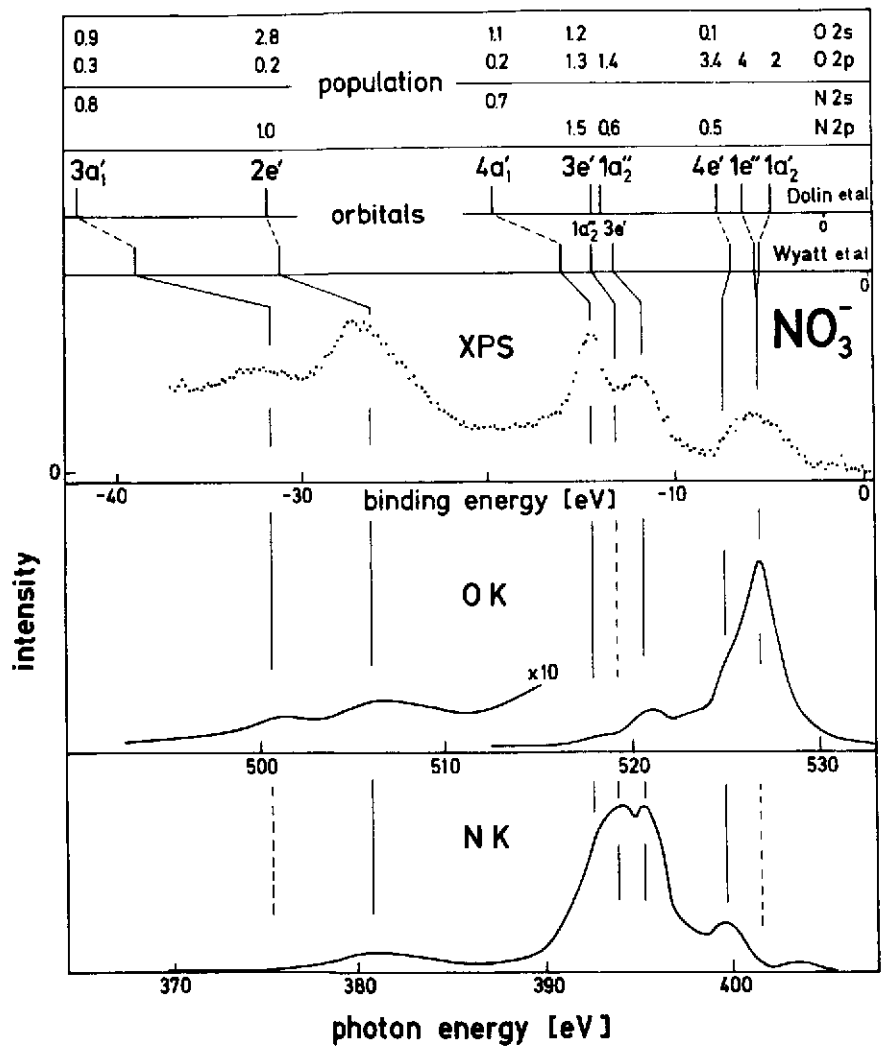


Fig. 2

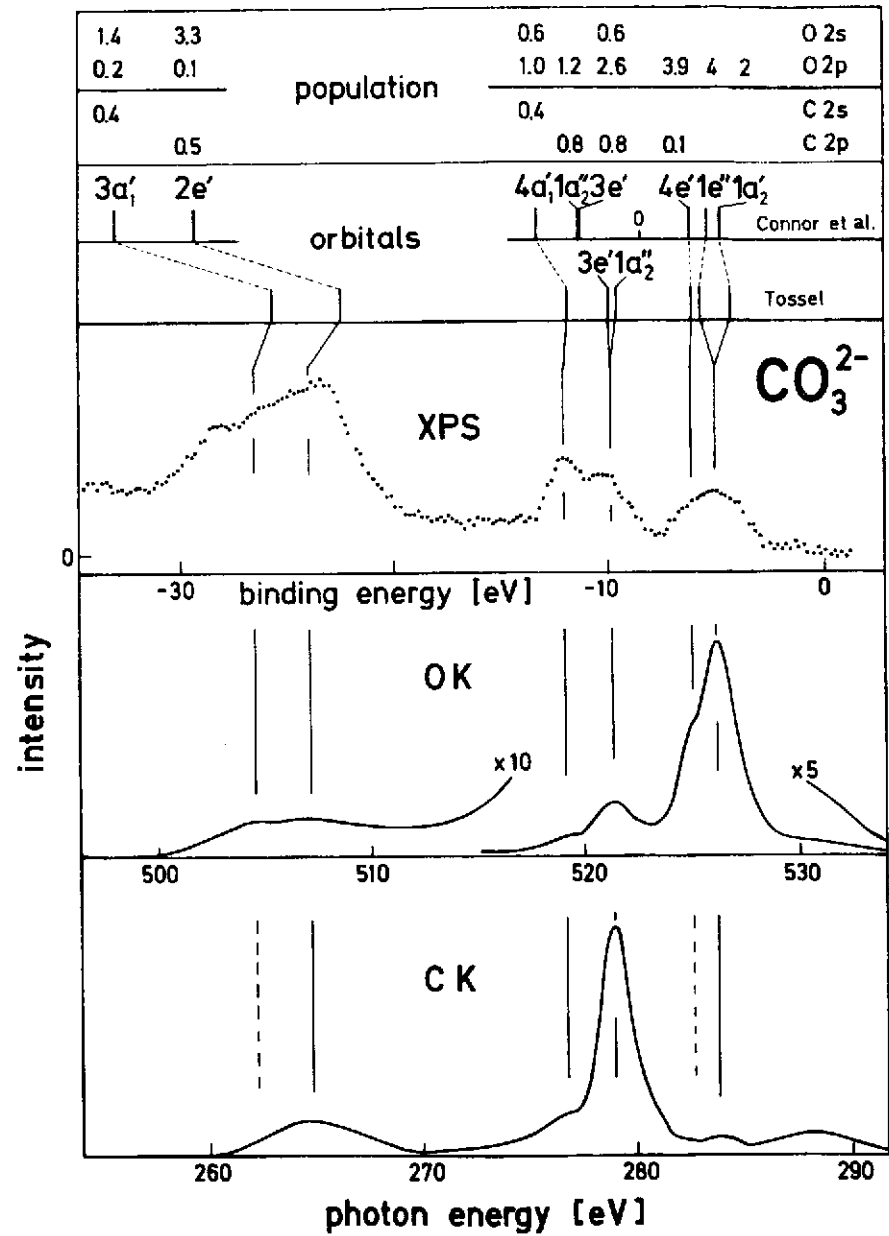


Fig. 3