

INVESTIGATION INTO THE STRUCTURES OF NITRITE AND NITRATE IONS

By

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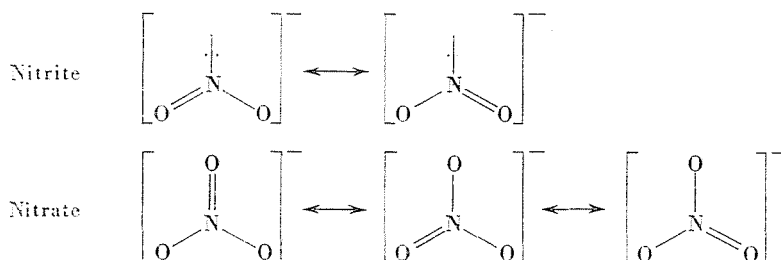
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Several authors have investigated the bond structures of nitrite and nitrate ions by infrared, Raman, ultraviolet and X-ray examinations [1—6].

The results of these works are widely known: the nitrogen—oxygen bond has the character of a partial double bond. In spite of this, the structure has not been subjected to any definitive, unequivocal examination. This also appears from the numerous forms of representation of nitrite and nitrate ions.

Most widely used are the boundary structures written on the basis of the VB method:



This way of representation seems to indicate as if, besides the σ bonding pairs, an electron pair π existed in the ions. This, however, is contradicted, besides other things, also by the results of ultraviolet examinations.

This is why, in our work, we started out from the experimental data of the ultraviolet spectrum. Several authors have recorded ultraviolet spectra of nitrite and nitrate ions under various conditions (various solvents, different types of apparatus, etc.). For the purpose of our calculations the taking of spectra in the course of our work was deemed necessary. Our measurements were carried out with an ultraviolet spectrophotometer type Spektromom 201, at 25 °C temperature, with the use of quartz cells of 1 cm path length. Concentrations of 10^{-1} to 10^{-5} mol/litre, with distilled water as a solvent, were applied. The measurement results are shown in Fig. 1 and listed in Table I.

Table I

Wavelengths (λ), wave numbers (ν^*) and extinction coefficients (ϵ), belonging to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of nitrite and nitrate ions

	$\pi \rightarrow \pi^*$			$n \rightarrow \pi^*$		
	λ (nm)	ν^* (cm ⁻¹)	ϵ	λ (nm)	ν^* (cm ⁻¹)	ϵ
NO ₂ ⁻	200	50 000	13 500	302	33 100	7
NO ₃ ⁻	210	47 600	5 500	355	28 170	25

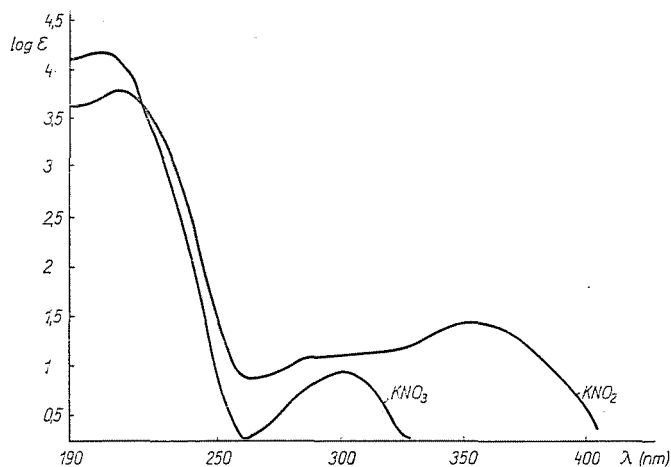


Fig. 1

Table I lists the wavelengths (λ , nm), the wave numbers (ν^* , cm⁻¹) and extinction coefficients (ϵ), belonging to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

From the work of ORVILLE-THOMAS and JONES [7] it is known that LCAO—MO parameter calculations can be made also for molecules composed of heterogeneous atoms.

For the Hückel parametric solution the parametric forms of the Coulomb integral (α_i) and of the resonance integral (β_{ij}) are needed.

$$\alpha_i = \int \varphi_i H \varphi_i d\tau = \alpha + h_i \beta \quad (1)$$

$$\beta_{ij} = \int \varphi_i H \varphi_j d\tau = k \cdot \beta = \frac{S_{ij}}{S_0} \beta = 0.7 \beta \quad (2)$$

where

φ_i and φ_j are eigenfunctions of the i th and j th atomic orbitals
 H = Hamiltonian operator

- α = Coulomb integral of the carbon atom in benzene
 β = resonance integral of carbon-carbon atomic orbital in benzene
 S_{ij} = overlap integral of the i th and j th atomic orbitals
 S_0 = overlap integral of the carbon-carbon atomic orbitals
 $\frac{S_{ij}}{S_0} = 0.7$ as found in literature.

According to ORVILLE-THOMAS and JONES:

$$h_i = \left(\frac{X_i}{X_c} - 1 \right) \cdot \frac{\alpha}{\beta} = \left(\frac{X_i}{X_c} - 1 \right) \cdot 4.1 \quad (3)$$

where X_i is the electronegativity of the i atom, and X_c that of the carbon atom, to be calculated according to GORDY and ORVILLE-THOMAS [8] from the formula:

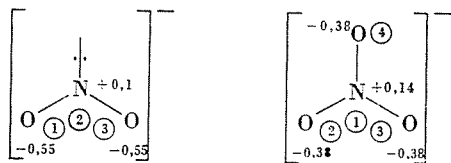
$$X_i = 0.31 \left(\frac{n + 1 + \delta}{r} \right) + 0.50 \quad (4)$$

where

- n = number of peripheral electrons on the neutral atom
 δ = formal charge
 r = simple covalent radius.

Formula (4) assumes the knowledge of δ ; according to literature [9], relatively the oxygen in the N—O bond is -0.05 .

On this basis the formulae of the partial charge ratios of NO_2^- and NO_3^- ions, needed for the starting step of the calculations, can be written as



1. Nitrite ion (NO_2^-)

From formulae (3) and (4) the electronegativities (X_i) and the Coulomb integral parameters (h_i) can be calculated. Their values are given in Table II.

As NO_2^- is of the symmetry C_{2v} , the determinant of the third order formed of its matrix may be broken up into a determinant of the first order and one of the second order. The solutions of these determinants give the eigenvalues.

$$\begin{vmatrix} \alpha + h_0 \beta - \varepsilon & \sqrt{2} \beta_{\text{NO}} \\ \sqrt{2} \beta_{\text{NO}} & \alpha + h_{\text{N}} \beta - \varepsilon \end{vmatrix} = 0 \quad (5)$$

(6)

Table II

Data of nitrite ion needed for LCAO—MO calculation

X_N	3.0554	h_N	0.9106
X_O	3.2020	h_O	1.1513

$$\beta_{NO} = 0.7\beta$$

If

$$\frac{\alpha - \varepsilon}{\beta} = y$$

equations (5) and (6) then give three roots for y (y_1, y_2, y_3), from which the eigenvalues may be calculated in turn:

$$\varepsilon_i = \alpha - y_i \beta \quad (7)$$

From (5) and (6) the eigenvalues, the linear coefficients (c_i), the electron density values (q_i):

$$q_i = 2 c_i^2 \quad (8)$$

and the partial charge ratios (δ_i):

$$\delta_i = 1 - q_i \quad (9)$$

can be calculated. The partial charge ratios δ_i thus obtained can be used on the basis of (3) and (4) to improve the Coulomb integrals and with the ω technique [10] the calculation may be refined. Calculations were made for the fourth approximation; the results are listed in Table III.

Table III

Results of approximations regarding the nitrite ion

Number of approximations	y_1	y_2	y_3	δ_N	δ_O
0	-2.0282	-1.1513	-0.0338	+0.1208	-0.5604
1	-2.0329	-1.1367	-0.0434	+0.0988	-0.5496
2	-2.0277	-1.1519	-0.0331	+0.1218	-0.5610
3	-2.0333	-1.1359	-0.0437	+0.0980	-0.5490
4	-2.0290	-1.1450	-0.0345	+0.1158	-0.5458

The results have given a divergent series, from which the final values were obtained by extrapolation. The final values are assembled in Table IV listing the eigenvalues (ϵ), the linear coefficients ($C_{O(1)}$, $C_{N(2)}$, $C_{O(3)}$) and the numbers of electrons at each energy level (e).

Table IV
Final computation results regarding the nitrite ion

ϵ_i	$C_{O(1)}$	$C_{N(2)}$	$C_{O(3)}$	e
$\epsilon_1 = \alpha + 2.0290\beta$	0.5280	0.6649	0.5280	2
$\epsilon_2 = \alpha + 1.1450\beta$	0.7071	0.0000	-0.7071	2
$\epsilon_3 = \alpha + 0.0345\beta$	-0.4706	0.7464	-0.4706	0

Thus the general form of the eigenfunction can be written as

$$\Psi_{\text{NO}_2^-} = C_{O(1)}\varphi_{O(1)} + C_{N(2)}\varphi_{N(2)} + C_{O(3)}\varphi_{O(3)}$$

Let us use the linear coefficients to calculate the order of the bond:

$$p = 2 \sum_{i=1}^{l=k} C_{ii} C_{ij} \quad (10)$$

where the summation is performed only for the filled levels (up to k).

From the order of the bond, on the other hand, the distance of bonds may be calculated by using the COULSON formula [11]:

$$R = R_1 - (R_1 - R_2) \frac{3p}{2p + 1} \quad (11)$$

where

$$R_1 = \text{distance of simple NO bond} = 1.41 \text{ \AA}$$

$$R_2 = \text{distance of double NO bond} = 1.19 \text{ \AA} \quad [12]$$

The results of the calculations relating to the nitrite ion are summed up in Table V.

Table V

Molecular structure constants of the nitrite ion. A comparison of our calculations with data found in literature

	δ_N	δ_O	p	$R(\text{\AA})$
Calculated	+0.1158	-0.5458	0.702	1.22
Found in literature	+0.1000 ^[9]	-0.5500 ^[9]	—	1.23 ^[12]
Difference	-0.0158	+0.0042	—	+0.01

2. Nitrate ion (NO_3^-)

The starting data were calculated with the method discussed in relation to the nitrite ion. They are listed in Table VI.

Table VI
Data of nitrate ion needed for LCAO—MO calculation

X_N	3.0721	h_N	0.9381
X_O	3.2732	h_O	1.2677

$$\beta_{\text{NO}} = 0.7\beta$$

As the nitrate ion belongs to the symmetry class C_{3v} , the determinant of the fourth order formed from the matrix can be broken up into a determinant of the second order and two identical determinants of the first order. The first determinant yields two eigenvalues, and the other two determinants give two eigenvalues.

The determinant of the second order can be written as

$$\begin{vmatrix} \alpha + h_0\beta - \varepsilon & \sqrt{3}\beta_{\text{NO}} \\ \sqrt{3}\beta_{\text{NO}} & \alpha + h_N\beta - \varepsilon \end{vmatrix} = 0 \quad (12)$$

Let

$$y = \frac{\alpha - \varepsilon}{\beta}$$

the eigenvalues can be calculated from (7). From the above it follows that there are two degenerated levels, $\alpha_0 = \alpha + h_0\beta$.

Thus four eigenvalues (y_1, y_2, y_3 and y_4) are obtained. With the ω technique used also for the nitrite ion, carrying the calculations to the fourth approximation, the results listed in Table VII are obtained.

In this case the values were found to be convergent. The final results were obtained by extrapolation also here (Table VIII).

The forms of the eigenfunctions for the nitrate ion are:

$$\Psi_{\text{NO}_3^-} = C_{\text{N}(1)}\varphi_{\text{N}(1)} + C_{\text{O}(2)}\varphi_{\text{O}(2)} + C_{\text{O}(3)}\varphi_{\text{O}(3)} + C_{\text{O}(4)}\varphi_{\text{O}(4)}$$

By using the data thus obtained, the order of the bond can be calculated from (10), and the distance from (11). For the data cf. Table IX.

Table VII

Results of approximations regarding the nitrate ion

Number of approximations	y_1	y_2	y_3	y_4	δ_N	δ_O
0	-2.3265	-1.2677	-1.2677	+0.1207	+0.1348	-0.3781
1	-2.3249	-1.2704	-1.2704	+0.1237	+0.1388	-0.3795
2	-2.3262	-1.2684	-1.2684	+0.1214	+0.1358	-0.3785
3	-2.3251	-1.2698	-1.2698	+0.1231	+0.1378	-0.3791
4	-2.3257	-1.2691	-1.2691	+0.1221	+0.1370	-0.3785

Table VIII

Final calculation results regarding the nitrate ion

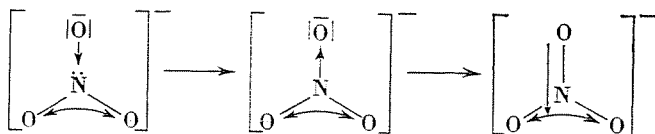
ϵ_i	$C_{N(1)}$	$C_{O(2)}$	$C_{O(3)}$	$C_{O(4)}$	e
$\epsilon_1 = \alpha + 2.3257\beta$	0.6569	0.4352	0.4352	0.4352	2
$\epsilon_2 = \alpha + 1.2691\beta$	0.0000	0.8164	-0.4082	-0.4082	2
$\epsilon_3 = \alpha + 1.2691\beta$	0.0000	0.0000	0.7071	-0.7071	2
$\epsilon_4 = \alpha - 0.1221\beta$	-0.7536	0.3792	0.3792	0.3792	0

Table IX

Molecular structure constants of the nitrate ion
A comparison of our calculations with data found in literature

	δ_N	δ_O	P	$R(\text{\AA})$
Our calculations	+0.1370	-0.3785	0.572	1.23
Found in literature	+0.1400 ^[9]	-0.3800 ^[9]	—	1.22 ^[12]
Difference	+0.0030	+0.0015	—	-0.01

True values for the partial charges will be obtained only if it is assumed that the formation of a nitrate ion from a nitrite ion goes through the donation of the single electron pair σ of the nitrogen to an oxygen atom:



while the electron pair π of the same oxygen atom is donated to the nitrogen. At the instant of the production of the ion it may be assumed that the entering oxygen is partially positive with respect to the bond π , that is, after the dislocation has taken place all three oxygen atoms become identical. The method of calculation of the partial charge ratio is illustrated in working out of the data of the third approximation (Table X). In this case the partial charge ratio was calculated in the following way:

Table X

Method of calculation of partial charge ratio

	N	O	O	O
q_i	0.8622	1.7124	1.7124	1.7124
q_i^0	1	1	1	2
δ_i^*	0.1378	-0.7124	-0.7124	+0.2876
δ_i	0.1378	$\frac{2(-0.7124) + 0.2876}{3} = -0.3791$		

In the table

q_i^0 = the p -electron density of the neutral atom

δ_i^* = "apparent" partial charge

The data thus obtained permit the calculation of the relative energies belonging to the transitions $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ of nitrite and nitrate ions. On the basis of the data listed in Tables IV and VIII, the energy levels of the molecular orbitals of nitrite and nitrate ions can be represented in terms of β units, as shown in Fig. 2, with the indication of the n levels.

Table XI

Experimental and calculated values belonging to
 $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of nitrite and nitrate ions

	NO ₂ ⁻		NO ₃ ⁻	
	Experimental	Calculated	Experimental	Calculated
$\pi \rightarrow \pi^*$	47 600 cm ⁻¹	1.1105 β	50 000 cm ⁻¹	1.3912 β
$n \rightarrow \pi^*$	28 170 cm ⁻¹	0.7108 β	33 100 cm ⁻¹	0.8674 β
$\frac{\pi \rightarrow \pi^*}{n \rightarrow \pi^*}$	1.689	1.562	1.510	1.603

It should be noted here that the simple LCAO method cannot give in an exact way the values belonging to the transitions. As it does not take the interactions of the electrons into consideration, it can yield only mean values belonging to triplet and singlet transitions.

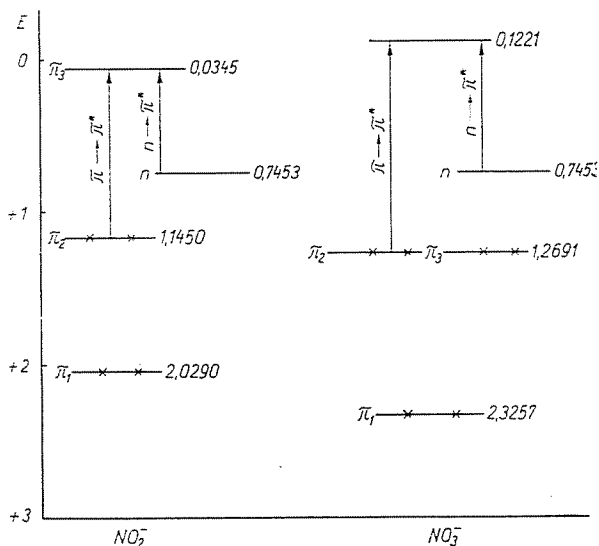


Fig. 2

In Fig. 2 it can be seen that in the dislocated π bond in the case of a nitrite ion four electrons, and in the case of a nitrate ion six electrons take part. This fact defines the values of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions that can be calculated on the basis of the eigenvalues (Table XI).

The calculation results show a fair correlation with the experimental data, and, in compliance with the latter, the nitrite ion displays a bathochromic effect with respect to the nitrate ion.

In another step of the work the oscillator strength (f) has been determined. The oscillator strength can be calculated from UV spectra by means of the following empirical formula [13]:

$$f = 4.32 \cdot 10^{-9} \varepsilon_{\max} \Delta\nu^* \quad (13)$$

where

ε_{\max} = the maximum extinction coefficient belonging to the transition,

$\Delta\nu^*$ = the band width found at the value of $\frac{\varepsilon_{\max}}{2}$

Theoretically the oscillator strength can be calculated in the following way:

$$f = 1.085 \cdot 10^{-5} \nu^* \cdot D \cdot G \quad (14)$$

where

ν^* = wave number corresponding to the transition

$$D = Q_x^2 + Q_y^2 + Q_z^2$$

$$Q_q = \sqrt{2} \int \Psi_m \Sigma q \Psi_n d\tau$$

q = coordinates x, y, z

G = degeneration grade of ultimate state.

Here Ψ_m is the eigenfunction belonging to the ground state, and Ψ_n that belonging to the excited state.

The results are listed in Table XII.

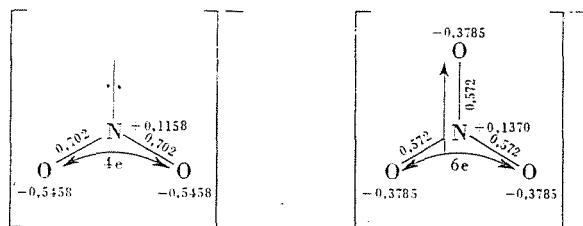
Table XII

Oscillator strength of nitrite and nitrate ions

	$f_{\text{calcul.}}$	$f_{\text{exper.}}$	ν^* (cm ⁻¹)
NO ₂ ⁻	0.5101	0.147	47 600
NO ₃ ⁻	0.3482	0.484	50 000

The calculations have demonstrated that $\pi \rightarrow \pi^*$ transitions are not inhibited; with the nitrite ion they appear polarized along one of the axes, with the nitrate ion they are polarized in a plane.

As resulting from our calculations, the structures of nitrite and nitrate ions may be represented in the following way



The formulae indicate the partial charge ratios, the orders of the bonds and the numbers of dislocated π electrons.

Summary

1. To calculate the molecular structures of nitrite and nitrate ions ultraviolet spectra have been taken.

2. By using the HÜCKEL method and the ORVILLE-THOMAS—JONES method, and with the application of the LCAO—MO technique, the eigenvalues, partial charges, bond orders, bond distances, energy values belonging to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, as well as the oscillator strengths of nitrite and nitrate ions have been calculated. The results show a fair agreement with the experimental data.

3. On the basis of the experimental results it can be stated that in the case of nitrite four electrons, and in the case of nitrate six electrons take part in the dislocated π bond; in the case of a nitrate ion two degenerated, non-bonding levels result.

References

1. MOOKHERJI, A., TANDON, S. P.: Indian J. Phys. **36**, 211 (1962)
2. MOOKHERJI, A., TANDON, S. P.: Indian J. Phys. **36**, 344—50 (1962)
3. MEYERSTEIN, D., TREININ, A.: Trans. Farad. Soc. **57**, 2104 (1961)
4. SAYRE, E.: J. Chem. Phys. **31**, 73 (1959)
5. MC. GLYNN, K.: J. Chem. Phys. **24**, 481 (1956)
6. SCHUTTE, C. J. H.: Z. Phys. Chem. **39**, 241 (1963)
7. ORVILLE-THOMAS, W. T., JONES, W. J.: Zeitschrift f. Elektrochemie No. 5, 714 (1960)
8. GORDY, W. J., ORVILLE-THOMAS, W. T.: J. Chem. Phys. **24**, 439 (1956)
9. SANDERSON: Chemical Periodicity. Reinhold Publ. Corp. New York (1960) 106.
10. STREITWIESER, A.: Molecular Orbital Theory. John Wiley, New York (1962) 115.
11. STREITWIESER, A.: Molecular Orbital Theory. John Wiley, New York (1962) 167.
12. WELLS, A. F.: Structural Inorganic Chemistry. Clarendon Press, Oxford (1962) XVI.
13. JAFFE, H. H., ORCHIN, M.: Theory and Applications of Ultraviolet Spectroscopy. John Wiley, New York (1962) VI.

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