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**NITROGEN 1s ELECTRON BINDING ENERGIES.
CORRELATION WITH CNDO CHARGES**

Jack M. Hollander, David N. Hendrickson and William L. Jolly

June 1968

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Nitrogen 1s Electron Binding Energies.

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Correlation with CNDO Charges. *

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Recent developments in photoelectron spectroscopy have made
possible the measurement of chemical shifts in inner-electron binding

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energies.¹ Binding energies for 1s electrons have been correlated with

¹ K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren and B. Lindberg, "ESCA Atomic Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksell's AB, Stockholm (1967).

formal oxidation state in sulfur^{1,2} and chlorine^{1,3} compounds and with

² A. Fahlman et al., Nature, 210, 4 (1966).

³ A. Fahlman et al., Arkiv Kemi, 25, 301 (1966).

fractional atomic charge (calculated by a modification of Pauling's method⁴)

⁴ L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell Univ. Press, Ithaca, N.Y., 1960, p. 97.

in sulfur¹ and nitrogen compounds.^{1,5} We have extended the group of nitrogen

⁵ R. Nordberg et al., Nature, 214, 481 (1967); R. Nordberg et al., Arkiv Kemi, 28, 257 (1968).

compounds for which nitrogen 1s binding energies have been measured and have shown that these binding energies are linearly related to nitrogen

atomic charges calculated from CNDO molecular orbital eigenfunctions.⁶

⁶ J. A. Pople, D. P. Santry, and G. A. Segal, J. Chem. Phys., 43, 5130 (1965). A modified CNDO/1 version involving empirically evaluated repulsion integrals was used, as per P. M. Kuznesof and D. F. Shriver, J. Am. Chem. Soc., 90, 1683 (1968). The authors wish to thank Dr. Paul Kuznesof for his helpful discussions regarding the calculations.

The CNDO method has been thoroughly checked only for compounds of elements lighter than neon, and therefore at this time we are reporting only the data for such nitrogen-containing compounds.

The experimental and theoretical aspects of the determination of inner-electron binding energies have been reviewed by Siegbahn et al.¹ The binding energy (the difference in energy between the Fermi level and the 1s atomic level for the solid) is calculated by the relation

$$E_b = E_{h\nu} - E_{kin} - \phi_{sp}$$

where $E_{h\nu}$ is the incident photon energy, E_{kin} is the kinetic energy of the photoelectron as it enters the spectrometer chamber, and ϕ_{sp} is the work function of the spectrometer material. We used magnesium K_{α} x-rays (1253.6 eV.) and an iron-free double-focusing magnetic spectrometer of 50-cm. radius.⁷ The work function of the spectrometer was determined to

⁷ J. M. Hollander, M. D. Holtz, T. Novakov, and R. L. Graham, Arkiv Fysik, 28, 375 (1965); T. Yamazaki and J. M. Hollander, Nuclear Physics, 84, 505 (1966).

be 4.0 eV. by using several of the compounds studied by Siegbahn et al.¹ as calibration standards. Spectrometer samples were prepared by brushing powdered solids onto double-backed conducting adhesive tape mounted on an aluminum plate.

The experimental binding energies and the CNDO calculated nitrogen atom charges are given in Table I. The data are plotted in Figure 1. It will be noted that the points seem to fall on two lines - one characteristic of anions, and the other characteristic of neutral molecules and possibly cations (although insufficient data are available to show definitely that the cation points fall on the same line as the neutral molecule points). The observance of separate lines for anions and neutral species can be rationalized by the fact that anions in an ionic crystal lattice experience a greater positive lattice potential than neutral molecules in a molecular lattice. It may be that the separate lines are an artifact of the CNDO method for calculating atomic charges.

A second feature of the plot is that all the data are reasonably well correlated; that is, there are no large discrepancies as were found in a previous attempt to correlate binding energies with charges calculated by Pauling's method.^{1,5} Because of this better fit of the data, we conclude that the atomic charges calculated by the CNDO method are better approximations to the true charges than those calculated by Pauling's method. By combining a plot such as Figure 1 with 1s binding energy data for compounds of uncertain structure it should be possible to estimate atomic charges and thus obtain useful structural information. Work along these lines is underway.

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Table I.

Nitrogen 1s Binding Energies and Calculated Charges

Compound		Calculated Nitrogen	
Number	Compound	Binding Energy, eV.	Atom Charge
1	NaNO ₃	407.4	+ 0.429
2	NaNO ₂	404.1	+ 0.100
3	Na ₂ [O $\overset{\sim}{\text{N}}$ NO ₂]	403.9	+ 0.140
3	Na ₂ [O $\overset{\sim}{\text{N}}$ NO ₂]	400.9	- 0.195
4	Na[$\overset{\sim}{\text{N}}$ NN]	403.7	+ 0.096
4	Na[$\overset{\sim}{\text{N}}$ NN]	399.3	- 0.548
5	Na ₂ N ₂ O ₂	401.3	- 0.256
6	KCN	399.0	- 0.518
7	KOCN	398.3	- 0.550
8	<u>p</u> -HOC ₆ H ₄ NO ₂	405.3 ^a	+ 0.353
9	C ₆ H ₅ NO ₂	405.1 ^a	+ 0.347
10	<u>n</u> -C ₅ H ₁₁ ONO	403.7 ^a	+ 0.288 ^b
11	N ₂ H ₆ SO ₄	402.5	+ 0.094
12	(CH ₃) ₃ NO	402.2 ^a	+ 0.079
13	$\overset{\sim}{\text{N}}$ H ₄ NO ₃	402.3	+ 0.039
14	(CH ₃) ₄ NB ₃ H ₈	402.2	+ 0.185
15	NH ₃ OHCl	402.1	+ 0.219

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