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NITROGEN 1s ELECTRON BINDING ENERGIES. CORRELATIONS WITH MOLECULAR ORBITAL CALCULATED NITROGEN CHARGES

David N. Hendrickson,[1] Jack M. Hollander[2] and William L. Jolly[1]

Contribution from the Department of Chemistry of the University of California and the Inorganic Materials Research and Nuclear Chemistry Divisions of the Lawrence Radiation Laboratory, Berkeley California, 94720

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Introduction

Extensive studies of chemical shifts associated with atomic core-electron binding energies have been made by Siegbahn *et al*[3] by use of the relatively new technique x-ray photoelectron spectroscopy. Measured binding energies have been correlated with formal oxidation states and with fractional atomic charges calculated by a modification of Pauling's method. We have recently reported preliminary results of a study of solid nitrogen compounds by x-ray photoelectron spectroscopy, and we have shown that the nitrogen 1*s* binding energies can be correlated with nitrogen atomic charges calculated from CNDO molecular-orbital eigenfunctions.[4]

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(3) 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," Almquist and Wiksells AB, Stockholm (1967).

(4) J. M. Hollander, D. N. Hendrickson, and W. L. Jolly, *J. Chem. Phys.*, *49*, 3315 (1968), and references therein.

In this paper we extend the correlation of the nitrogen 1*s* binding energy data to include atomic charges evaluated by the extended Hückel molecular orbital method. We use these correlations and the observed nitrogen 1*s* binding energies for sodium oxyhyponitrite ($Na_2N_2O_3$) to establish the structure of the $N_2O_3^{2-}$ ion. In addition, we use binding energy data for some nitrogen-containing metal-coordinated ligands to characterize the bonding in these ligands.

Experimental

Mg K_α x-radiation (1253.6 eV) was used. The kinetic energy of the photoelectrons was measured in an iron-free, double-focusing magnetic spectrometer[5] shown schematically in Figure 1. The instrumental line width, including the contribution from the x-ray line, was about 1 eV, and the observed photoelectron lines had widths of 1.5-2.5 eV. Photoelectrons were counted[6] typically for time intervals of 12 sec. at each magnetic field setting, and the spectrometer current in the range 1.0-1.5A was varied in increments of 0.2mA.

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(5) 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).

(6) A Bendix curved channel-multiplier ("Channeltron") was used as the electron detector.

The compounds studied were either purchased or prepared by standard syntheses. Spectrometer samples were prepared by brushing the powdered material onto double-faced conducting tape attached to an aluminum plate that served as a heat and electron sink. Three measurements were made for each sample; in each case the carbon 1s line (arising from pump oil which forms a film on the samples) was recorded. The film of pump oil provides a convenient reference peak and probably also acts to remove surface charging that may arise with insulating samples. By this method

it is possible to locate the photoelectron peaks reproducibly to within 0.2 eV.

The work function for the spectrometer material (aluminum) was assigned the value 4.0 eV. This normalization gives the best agreement of our nitrogen core-electron binding energies with previously measured values for the same nitrogen compounds, and makes it possible to include some of the binding energies of Siegbahn et al[3] in the correlations with our calculated charges.

Calculations

Molecular orbital eigenfunctions were obtained from CNDO[7] and extended Hückel[8] calculations. In both cases computations were performed

(7) J. A. Pople, D. P. Santry, and G. A. Segal, J. Chem. Phys., 43, S129, S136 (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).

(8) R. Hoffmann, J. Chem. Phys., 39, 1397 (1963).

with a CDC 6400 computer using a Fortran IV program. Calculational details and required input data for the CNDO calculations are given in Reference 7. In the extended Hückel calculations, the Coulomb integrals, H_{ii}, were approximated by the valence state ionization potentials calculated by Hinze and Jaffé.[9] The arithmetic mean approximation for the off-diagonal elements of the H matrix was used:[10]

$$H_{ij} = 1.75\ S_{ij}\ (H_{ii} + H_{jj})/2$$

(9) J. Hinze and H. H. Jaffé, J. Am. Chem. Soc., 84, 540 (1962).

(10) M. Wolfsberg and L. Helmholz, J. Chem. Phys., 20, 837 (1952).

Here S_{ij} is the overlap integral between the ith and jth orbitals.

Net atomic charges were obtained by subjecting the extended Hückel molecular orbitals to a Mulliken population analysis.[11] In the CNDO method there is no overlap population, and as such the net atomic charges are easily obtained from the appropriate diagonal elements of the charge density matrix.

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(11) R. S. Milliken, J. Chem. Phys., 23, 1833, 1841, 2338, 2343 (1955).

Cartesian coordinates for complicated systems were obtained from program PROXYZ,[12] coupled with experimental[13] or estimated molecular parameters.

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(12) P. M. Kuznesof, Quantum Chemistry Program Exchange (Indiana University), QCPE 94 (1966).

(13) "Table of Interatomic Distances," L. E. Sutton ed., Special Publication No. 11, The Chemical Society, Burlington House, London, 1958, and No. 18, Supplement, 1965.

Theory

Because we are dealing with measurements on solid materials, the calculated electron binding energies are referred to the Fermi levels of the solids. We calculate the electron binding energies, E_b, from the relation[3]

$$E_b = E_{x\text{-}ray} - E_{kin} - \phi_{spec}$$

where $E_{x\text{-}ray}$ is the incident x-ray energy, E_{kin} is the kinetic energy of the photoelectron, and ϕ_{spec} is the work function of the spectrometer material, aluminum. The core-electron binding energies are dependent on the chemical environment, and previous discussions have shown that they are principally determined by the potential associated with the valence shell electron density and the crystal field felt by the core electrons.[3,14]

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(14) R. Nordberg, R. G. Albridge, T. Bergmark, U. Ericson, J. Hedman, C. Nordling, K. Siegbahn, and B. J. Lindberg, Arkiv. Kemi, 28, 257 (1968).

For binary salts, Siegbahn and co-workers[3,14] have formulated a relation between the electronic charge (q) removed from the valence shell of an atom and the energy shift (ΔE) of the core electrons of that atom:

$$\Delta E = \left(\frac{1}{r} - \frac{\alpha}{R}\right) q$$

Here r is the radius of the valence shell, and α is the contribution to the Madelung constant from the atom at the internuclear distance R. A relation is expected between the measured binding energy and the valence charge density.

Results and Discussion

Correlation with Atomic Charges - Extended Hückel calculations were completed for 28 nitrogen compounds; the calculated nitrogen atom charges and the measured nitrogen 1s binding energies are listed in Table I. Some binding energies determined in previous studies are also given with the corresponding calculated nitrogen charges. A linear correlation between 1s nitrogen binding energies and extended Hückel calculated nitrogen charges is demonstrated in Figure 2.

The range of nitrogen 1s binding energies covered by this correlation plot is approximately 10 eV, extending from the nitrate ion to pyridine. This is about the same range covered by Nordberg et al[12] in their correlation of nitrogen 1s binding energy with fractional atomic charge calculated by a modification of Pauling's method. In the case of our extended Hückel plot the correlation seems to be linear, whereas the correlation obtained by Nordberg et al shows curvature. In addition, the extended Hückel calculations assign charges to the nitrogens in n-amyl nitrite, nitrite ion, cyanide ion and azide ion that fit reasonably well on the line, whereas their fit on the modified Pauling plot is poor. It will be noted that the extended Hückel calculations give reasonably good fit for nitrogen molecules that contain sulfur or phosphorus atoms. In these cases it was found (See Table I) that inclusion of 3d orbitals on the sulfur or phosphorus atoms did not appreciably change the calculated nitrogen atom charges.

TABLE I.

Nitrogen 1s Binding Energies and Calculated Charges

Compound Number	Compound	Binding Energy, eV.	Calculated Nitrogen Atom Charge: CNDO	Calculated Nitrogen Atom Charge: Extended Hückel[γ]
1	$NaNO_3$	407.4	+0.429	+2.557
2	$NaNO_2$	404.1	+0.100	+1.273
3	$Na_2(ON\underset{\sim}{N}O_2)$	403.9	+0.140	+1.749
3	$Na_2(O\underset{\sim}{N}NO_2)$	400.9	-0.195	-0.090
4	$Na(\underset{\sim}{N}NN)$	403.7	+0.096	+1.066
4	$Na(\underset{\sim}{N}N\underset{\sim}{N})$	399.3	-0.548	-1.033
5	$Na_2N_2O_2$	401.3	-0.256	+0.175
6	KCN	399.0	-0.518	-1.181
7	KOCN	398.3	-0.550	-1.572
8	p-$HOC_6H_4NO_2$	405.3[a]	+0.353	+1.541
9	$C_6H_5NO_2$	405.1[a]	+0.347	+1.613
10	n-$C_5H_{11}ONO$	403.7[a]	+0.288[b]	+1.323[b]
11	$N_2H_6SO_4$	402.5	+0.094	+0.184
12	$(CH_3)_3NO$	402.2[a]	+0.079	+0.520
13	$\underset{\sim}{N}H_4NO_3$	402.3	+0.039	-0.145
13	$NH_4\underset{\sim}{N}O_3$	407.2	+0.429	+2.557
14	$(CH_3)_4NB_3H_8$	402.2	+0.185	-0.253

Compound Number	Compound	Binding Energy, eV.	Calculated Nitrogen Atom Charge: CNDO	Calculated Nitrogen Atom Charge: Extended Hückel
15	NH_3OHCl	402.1	+0.219	+0.612
16	$(CONH_2)_2$	400.0	-0.133	-0.550
17	$(NH_2)_2CNCN$	399.2(broad)	-0.17 to -0.31[c]	-0.71 to -1.56[c]
18	C_6H_5CN	398.4[a]	-0.226	-1.356
19	C_5H_5N	398.0[a]	-0.166	-1.098
20	KSCN	398.5		-1.672(-1.711)
21	$NH_3(s)$	398.8	-0.079	-0.914
22	S_4N_3Cl	399.6		-0.912, -1.03[d] (-0.915, -0.984)
23	NH_3SO_3	401.8		-0.262 (-0.307)
24	$C_6H_5CONH_2$	399.4	-0.238	-0.236
25	$(NPCl_2)_3$	399.5		-1.718 (-1.741)
26	$C_5H_5N \cdot HCl$	400.2	+0.035	-0.352
27	BN	398.2		-1.4[f]
28	$Na_3(PO_2NH)_3$	398.5		-0.971 (-1.058)[e]

a Data of Siegbahn *et al.*[3]

b Charge calculated for CH_3ONO, the structure of which is known.

c The four structurally-different nitrogen atoms of this molecule bear different calculated charges.

d There are two different nitrogen atoms.

e Calculated for $r_{p-n} = 1.50$Å.

[f] Treated approximately, see results and discussion section.

[g] Number in parenthesis is for case where 3d orbitals are included.

There are qualifications that need be stated regarding two of the compounds. In the case of boron nitride the graphite-like structure was only approximated; only 24 atoms were considered in calculating the charge on a central nitrogen atom. The crystal structure of compound 28, $Na_3(PO_2NH)_3$, has not been reported; we assumed a cyclic anion with the bond distances $r_{N-H} = 1.0\mathring{A}$ and $r_{P-O} = 1.5\mathring{A}$, coupled with two different P-N distances, 1.5 and $1.7\mathring{A}$ $\left(\text{cf } 1.65\mathring{A} \text{ for } r_{P-N} \text{ in } (NPCl_2)_3^{13}\right)$. The calculations of the nitrogen charges gave for these two cases -0.971 and -0.984, respectively (without considering 3d orbitals on the phosphorus atoms).

The nitrogen charges obtained from the extended Hückel calculations range from -1.7 to almost +2.6. This range is to be contrasted with the much smaller charge range calculated from the CNDO molecular orbitals which were obtained for the same molecules (See Table I). As noted earlier,[4] the CNDO correlation plot (Figure 3) shows two lines - one characteristic of anions, and the other characteristic of neutral molecules and possibly cations. Two rationalizations can be formulated: (a) the two lines are merely an artifact of the CNDO method due to an inherent overemphasis of electron repulsion in the CNDO calculations of anionic molecules; (b) the two lines are an indication of differing lattice potentials associated with a core-electron at either an anionic or neutral site.

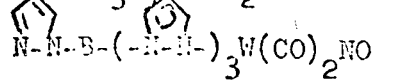
It is difficult at this time to indicate clearly the cause of the two CNDO lines. The fact that the extended Hückel data show no indication of the same behavior can probably only be taken as evidence of the simplicity of the latter calculations, at least insofar as this version

of the extended Hückel method is concerned. Previous work by Siegbahn and co-workers have shown that the expected differences in crystal potentials do not appear in the measured values (i.e., S_{2p} binding energies in a series of sulfates). This can also be seen in our N 1s data for the three nitrates, compounds 1, 13, and 29. Even further evidence for this lack of expected lattice potential influence can be seen in the data for the series of nitro-cobaltic ammines, compounds 47, 34, 37, 33, 34, and 36. Throughout this series the measured nitrogen 1s binding energy for either the coordinated NH_3 or NO_2^- is approximately constant. There is little evidence of discontinuity in the binding energies at the transition from a neutral to an anionic site.

Character of Metal-Coordinated Ligands - The power of the x-ray photoelectron method can be clearly seen in Figure 4, where we give the nitrogen 1s spectrum of trans $\left[Co(en)_2(NO_2)_2\right]NO_3$. Measurement of the nitrogen 1s binding energy of various metal-coordinated ligands can give insight into the character of the ligands. The binding energies of some metal-coordinated ammonia groups are listed in Table II. Comparison of these nitrogen binding energies with those obtained for the free ligand and for the ammonium ion (See Table I) as it exists in NH_4NO_3 shows that coordination of ammonia to Co(III), Rh(III), Ir(III), and Cr(III) gives partial ammonium-like character to the ammonia group. A similar result has been found for the triphenylphosphine ligand; the phosphorus 2p binding energies for coordinated triphenylphosphine and for a phosphonium ion were greater than for free triphenylphosphine.[15]

TABLE II.

Nitrogen 1s Binding Energies

Compound Number	Compound	Binding Energy(ev)
29	$[Rh(NH_3)_6]\underset{\sim}{N}O_3)_3$	407.3
30	trans $[Co(en)_2(NO_2)_2]\underset{\sim}{N}O_3$	406.8
31	$p\text{-}\underset{\sim}{N}O_2\text{-}C_6H_4CONH_2$	405.9
32	$[Rh(NH_3)_5\underset{\sim}{N}O_2]Br_2$	404.4
33	$Co(NH_3)_3(\underset{\sim}{N}O_2)_3$	404.1
34	$[Co(NH_3)_5\underset{\sim}{N}O_2]Cl_2$	404.0
35	$K[Co(NH_3)_2(\underset{\sim}{N}O_2)_4]$	404.0
36	$K_3Co(NO_2)_6$	404.0[a]
37	trans $[Co(NH_3)_4(\underset{\sim}{N}O_2)_2]SO_4$	403.9
30	trans $[Co(en)_2(\underset{\sim}{N}O_2)_2]NO_3$	403.8
38	$Na_2[Fe(CN)_5\underset{\sim}{N}O]\cdot 2H_2O$	403.3
39	S_4N_4	402.1
40	$[Co(NH_3)_5\underset{\sim}{N}O]Cl_2$	402.0
41	$C_6H_5NH_2NH_2\cdot HCl$	401.4[b]
42	$K_3[Cr(CN)_5\underset{\sim}{N}O]$	400.7
29	$[Rh(\underset{\sim}{N}H_3)_6](NO_3)_3$	400.7
43	$[Ir(NH_3)_5Cl]Cl_2$	400.6
44	 $N\text{-}N\text{-}B\text{-}(\text{-}N\text{-}N\text{-})_3W(CO)_2NO$	400.6[c]

Compound Number	Compound	Binding Energy(ev)
30	trans $[Co(en)_2(NO_2)_2]NO_3$	400.4
32	$[Rh(NH_3)_5NO_2]Br_2$	400.3
45	$S_4N_4 \cdot SbCl_5$	400.2
46	S_7NH	400.2
40	$[Co(NH_3)_5NO]Cl_2$	400.2
33	$Co(NH_3)_3(NO_2)_3$	400.2
35	$K[Co(NH_3)_2(NO_2)_4]$	400.0
34	$[Co(NH_3)_5NO_2]Cl_2$	400.0
47	$[Co(NH_3)_6]_2(SO_4)_3$	400.0
48	$[Co(NH_3)_5Cl]Cl_2$	400.0
37	trans $[Co(NH_3)_4(NO_2)_2]SO_4$	399.9
49	$Cr(NH_3)_6Cl_3$	399.9
31	$p\text{-}NO_2\text{-}C_6H_4CONH_2$	399.6
50	$S_4N_4H_4$	399.5
51	$(NPCl_2)_4$	399.2
52	$K_3[Cr(CN)_6]$	398.6
42	$K_3[Cr(CN)_5NO]$	398.4
38	$Na_2[Fe(CN)_5NO] \cdot 2H_2O$	398.2
53	P_3N_5	397.8
54	$K_4[Fe(CN)_6]3H_2O$	397.6
55	VN	397.2[d]
56	CrN	396.6

[a] A small peak attributable to nitrate impurity was observed at 407.0ev.

[b] Very broad peak.

[c] Only one relatively sharp peak observed.

[d] A decomposition product peak at 401.0ev was observed.

(15) M. Pelavin, D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, unpublished data.

In the case of the nitro ligand, however, the nitrogen 1s binding energies found for either $NaNO_2$ or for the metal-coordinated nitrite are approximately the same. Probably this can be explained by the metal-to-ligand π back-bonding operative in the metal-nitrite bond. This back-bonding would tend to keep the charge on the nitrogen atom approximately the same in the free and coordinated ligand. Considering the more extensive back-bonding expected in the metal-coordinated cyanide ion, it is heartening to see that the nitrogen 1s binding energy is appreciably lower for the cyanide coordinated to Fe(III), Cr(I) and Cr(III) than for the "free" cyanide in KCN.

Another problem which can be studied by the x-ray photoelectron method is the determination of the character of the NO group in various metal nitrosyls.[16]

(16) For review, see B. Johnson and J. McCleverty, "Nitric Oxide Compounds of Transition Metals" in Progress in Inorganic Chemistry, 7, 277 (1966).

There are four possible bonding situations: (a) lone pair donation to the metal from NO^+; (b) lone pair donation from NO with the odd electron retained by the NO; (c) lone pair donation from NO^-; (d) bridge bonding

as encountered in metal carbonyl compounds. The majority of metal nitrosyls are believed to be best formulated with the (a) type of bonding.

In Table II are listed the nitrogen 1s binding energies for two metal nitrosyl cyanides, $Na_2\left[Fe(CN)_5NO\right]\cdot 2H_2O$ and $K_3\left[Cr(CN)_5NO\right]\cdot H_2O$. It can be seen that the CN^- peak is relatively invariant to changes in the metal, whereas the NO peak shifts appreciably. This agrees with observations on the infrared spectra of these compounds;[17] that is, the CN stretching frequency is relatively unchanged as opposed to the large

(17) J. Lewis, R. J. Irving and G. Wilkinson, J. Inorg. Nucl. Chem., 7, 32 (1958).

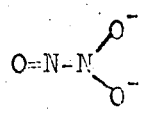
change for the NO stretch frequency from 1944cm^{-1} in the formally Fe(II) compound to 1645 cm^{-1} in the Cr(I) compound.[14] Both of these compounds have been formulated as NO^+ compounds,[17] but their NO nitrogen 1s binding energies clearly show that there is a marked difference in nitrogen charge in these two cases. It is a well-known fact that the NO^+ ligand has an empty π^* orbital available for back-bonding from the metal and further that back-bonding is greater in compounds with metals in lower oxidation states. The lower oxidation state in the case of the Cr(I) compound, indicating greater back-bonding, would be a possible explanation for the apparently less positive NO nitrogen in $Cr(CN)_5NO^{3-}$.

However, consideration of the measured NO binding energy for the formally Co(III) compound, $(Co(NH_3)_5NO)Cl_2$ (black isomer), indicates a certain predicament. This diamagnetic compound has been found to have a monomeric structure,[18] and the Co-N bond distance is reasonable for a

(18) D. Hall and A. A. Taggart, J. Chem. Soc., 1359 (1965); D. Dale and D. C. Hodgkin, J. Chem. Soc., 1364 (1965).

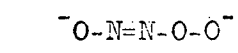
Co^{3+}-to-NO^- bond. The NO nitrogen in this cobalt compound would be expected then to possess the most negative nitrogen charge of these three nitrosyls, but if the binding energies are indicative, the cobalt compound is somewhat intermediate. Resolution of this problem will be best attained by carrying out more nitrogen binding energy measurements on metal nitrosyls, and possibly by studying the effective charges on the metal atoms.

Structure of the Oxyhyponitrite Ion - Perhaps the most remarkable demonstration in this study of nitrogen compounds is the clear proof of the existence of structurally different nitrogen atoms in the oxyhyponitrite ion, $N_2O_3^{2-}$. Various studies have been undertaken to differentiate between the possible structures of this ion, the three most probable structures being



I

II



III

Addison et al[19] concluded that the ulta-violet absorption spectrum of $N_2O_3^{2-}$ indicated an N=N bond. Calorimetric measurements[20] have suggested the structure I as most probable, and the infrared spectrum has been interpreted as having bands indicative of an $-NO_2$ grouping.[21] The

(19) C. C. Addison, G. A. Gamlen, and R. Thompson, J. Chem. Soc., 338 (1952).

(20) H. R. Hunt, J. R. Cox, and J. D. Ray, Inorg. Chem., 1, 938 (1962).

(21) R. D. Feltham, Inorg. Chem., 3, 900 (1964).

nitrogen 1s photoelectron spectrum of $Na_2N_2O_3$ (See Figure 5), with two resonances, clearly rules out structure II as a possibility. In order to distinguish between the two remaining structures, CNDO and extended Hückel calculations were completed for the two geometries (varying the N-N bond distance in each case). The net nitrogen charges obtained from the calculations are given in Table III. Structure I is indicated by these calculations; indeed structure III would be predicted to show only one peak, for the two different nitrogens are predicted to have approximately the same charge. Finally it can be seen in Figures 2 and 3 that the points representing structure I do fit the correlation lines. Recently the oxyhyponitrite ion has been shown by asymmetric ^{15}N-labelling to have two structurally-different nitrogen atoms.[22]

(22) D. N. Hendrickson and W. L. Jolly, Inorg. Chem., 8, 693 (1969).

TABLE III.

Calculated Nitrogen Charges for Two Asymmetric Oxyhyponitrite Structures

Structure	r_{N-N} (Å)	Calculated Nitrogen Charges* CNDO q_1	CNDO q_2	extended Hückel q_1	extended Hückel q_2
I	1.30	0.133	-0.151	1.75	0.040
	1.50	0.147	-0.239	1.75	-0.090
III	1.30	-0.158	-0.145	0.288	0.286
	1.50	-0.181	-0.188	0.198	0.254

* For each molecular orbital method the net nitrogen charges, q_1 and q_2, are given for the two structurally different nitrogen atoms in each structure.

FIGURE CAPTIONS

Figure 1 Schematic illustration of the experimental setup.

Figure 2 Plot of nitrogen 1s binding energies vs Extended Huckel-calculated charges on nitrogen atoms.

Figure 3 Plot of nitrogen 1s binding energies vs CNDO calculated charges on nitrogen atoms

Figure 4 Nitrogen 1s photoelectron spectrum for Trans $(Co(NH_2CH_2CH_2NH_2)_2(NO_2)_2)NO_3$.

Figure 5 Nitrogen 1s photoelectron spectrum for $Na_2N_2O_3$. Sodium nitride impurity[22] accounts for excess area in the higher binding energy peak.

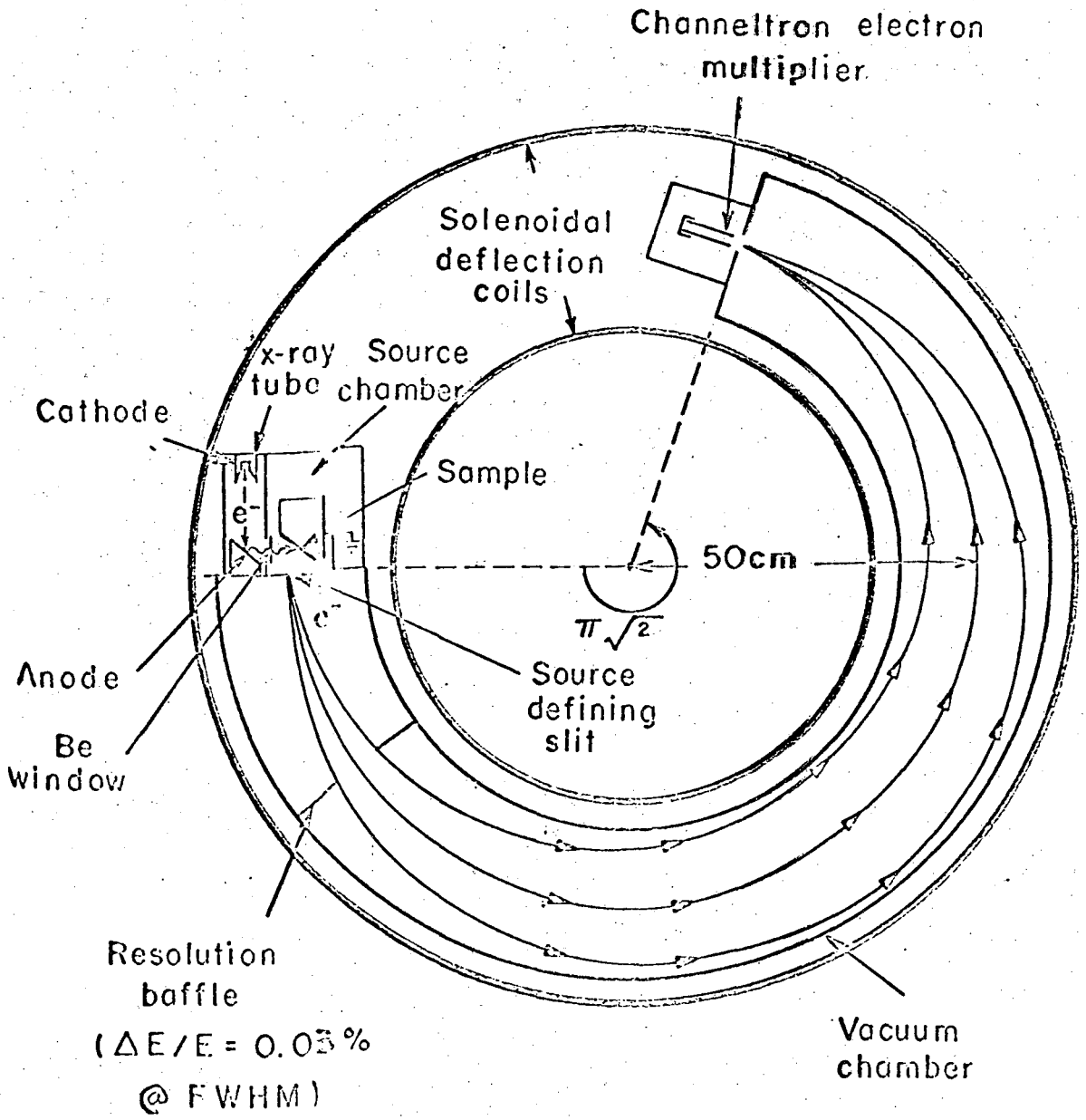
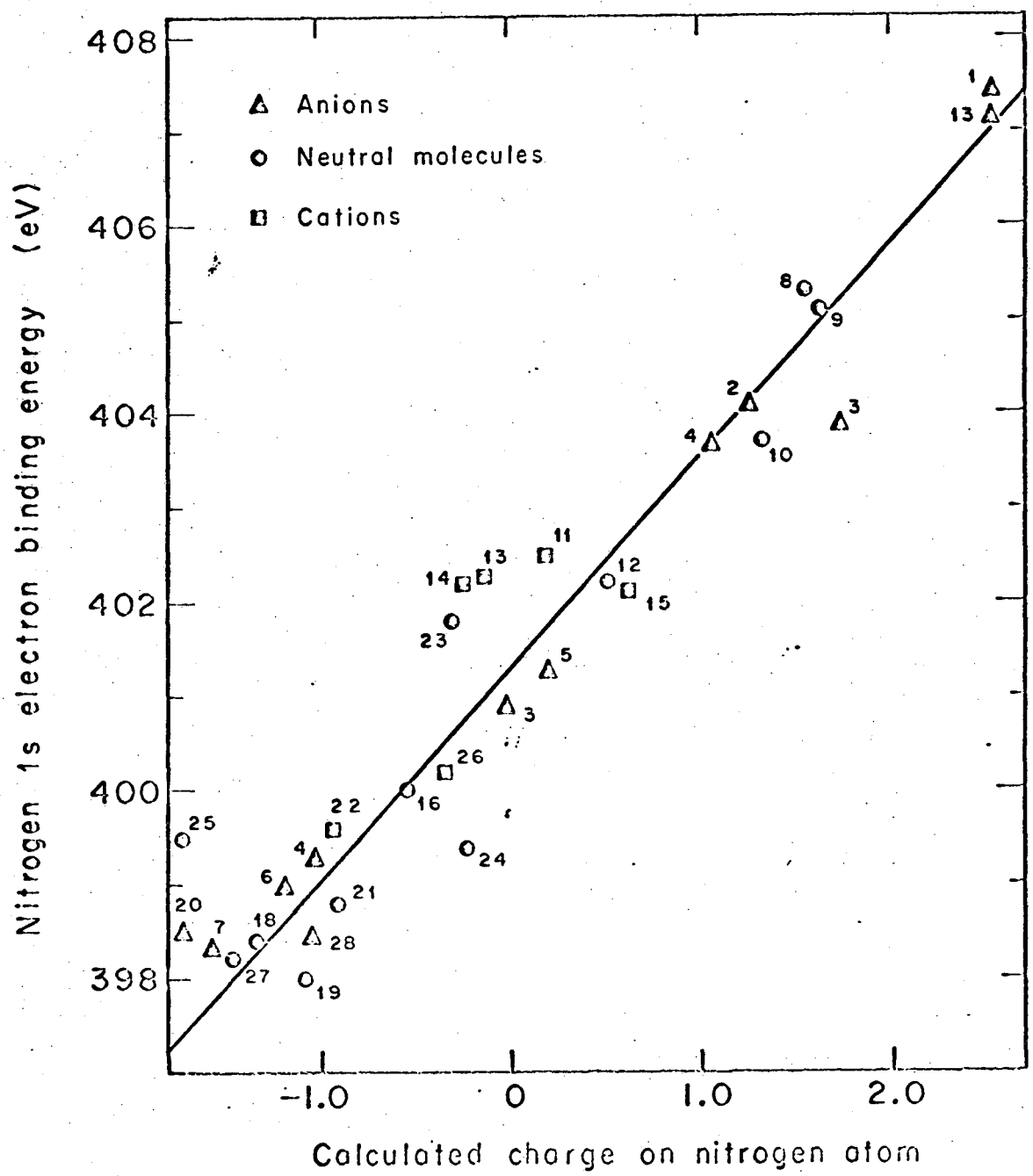


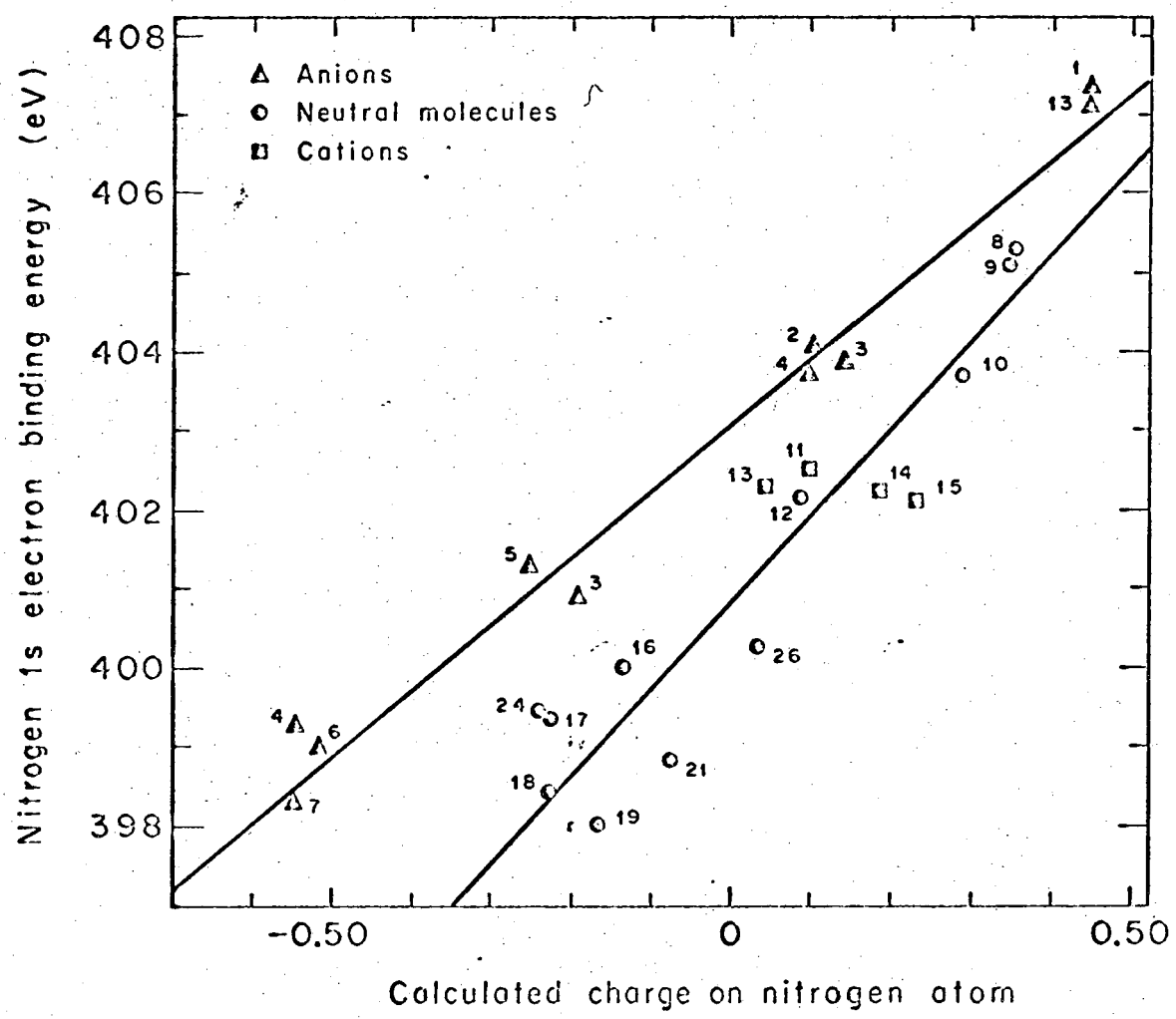
Fig. 1

XBL694-2402



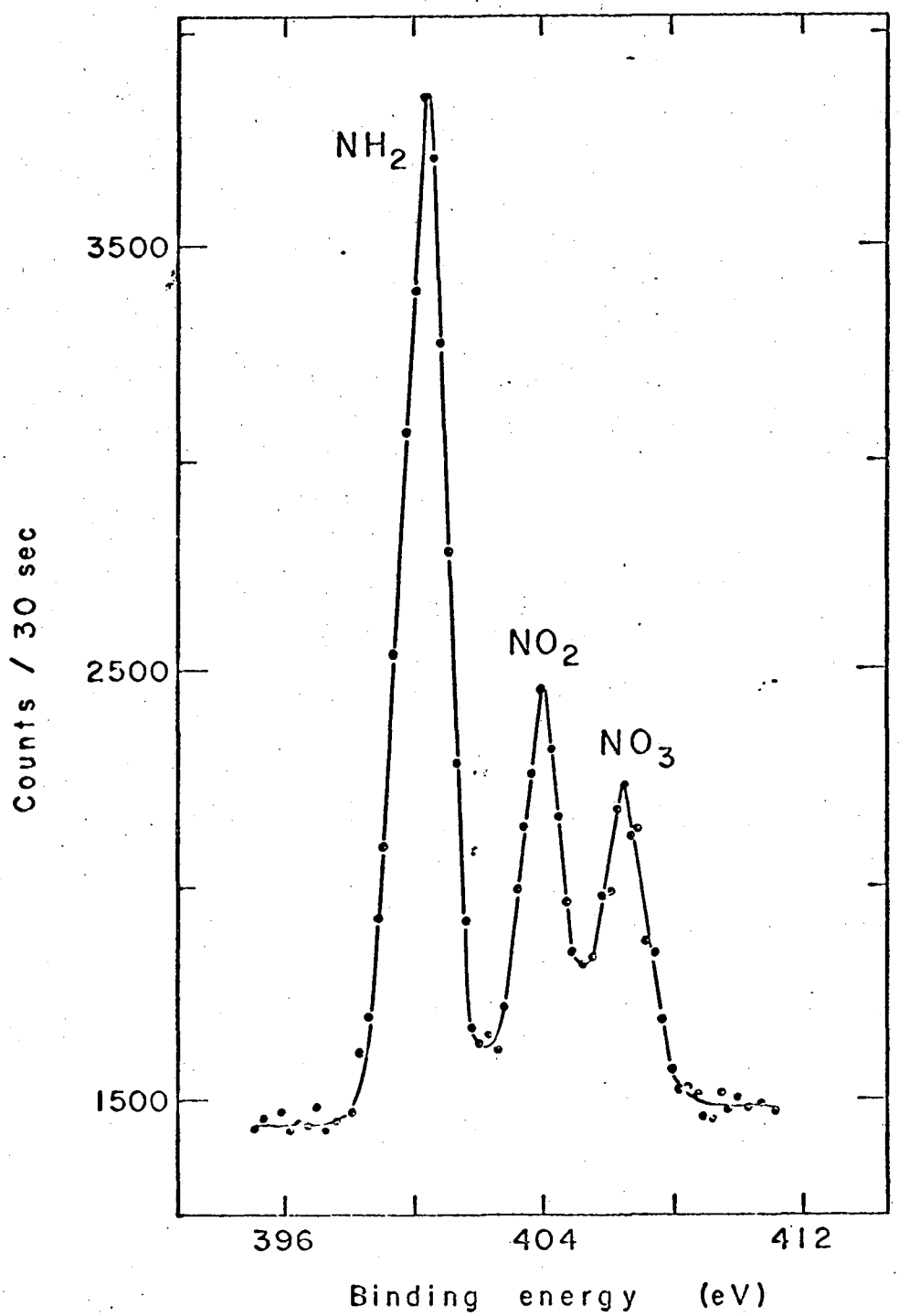
XBL695-2645

Fig. 2



XBL695-2642

Fig. 3



XBL695-2643

Fig. 4

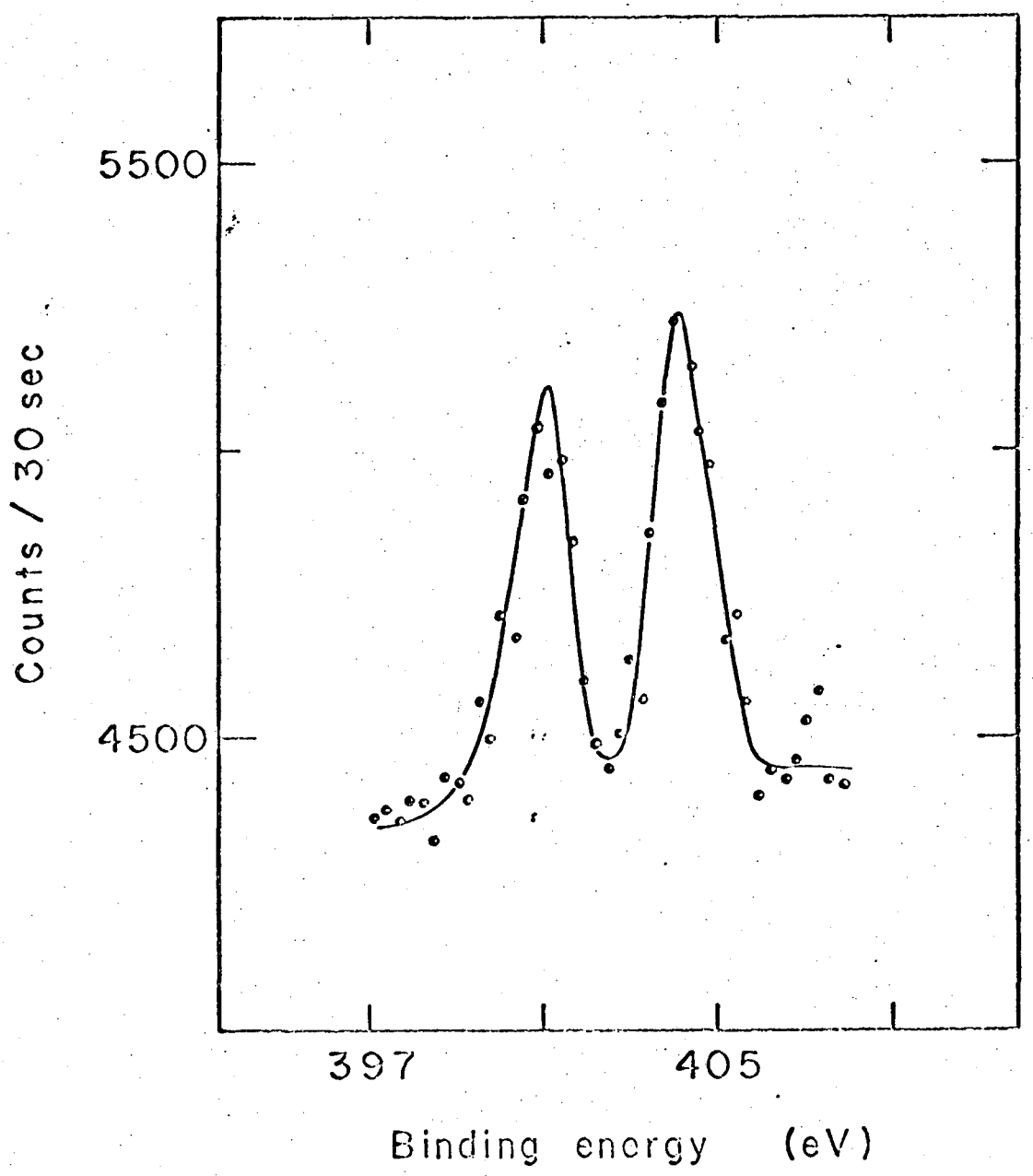


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Fig. 5

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