Submitted to Journal of Inorganic Chemistry

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May 1970

AEC Contract No. W-7405-eng-48

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Chemical Shifts in Core Electron Binding Energies for Some Gaseous Nitrogen Compounds

by Patricia Finn[1], Richard K. Pearson,[2]
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Chemical shifts in core electron binding energies for gaseous nitrogen compounds are compared with values estimated by various theoretical and empirical methods. The relative merits of these methods are discussed.

X-ray photoelectron spectroscopy is of great interest to chemists because the measured core electron binding energies are a function of the chemical environment of the atoms--that is, the binding energies show chemical shifts. Experimental binding energies for compounds of a given element can be estimated from (1) correlations with calculated atomic charges,[4-9] (2) thermodynamic data based on the approximation that the energy of core-electron capture by a nucleus is independent of chemical environment,[10-12] (3) empirical parameters characteristic of the directly bonded groups,[11] and (4) molecular orbital-calculated binding energies.[9,13-15]

In order to appraise the relative usefulness of the various methods of estimating chemical shifts, it is important to have chemical shifts that span a wide energy range. We chose to study compounds of nitrogen because of the wide variety of bonding types that they possess and the probability that they would yield a wide range of chemical shifts. We found that the estimation methods that were most readily tested with our data were the atomic charge correlation method and the thermodynamic method. The empirical group parameter method could only be partially tested with our data because, in the set of compounds we studied, many of the groups bonded to nitrogen atoms are unique to those nitrogen compounds. Molecular orbital-calculated binding energies are available for only a few of the compounds we studied; however, we hope that the availability of the experimental data will encourage others to make the further calculations required for a complete comparison.

In this paper we report data only for gaseous nitrogen compounds. Although many successful correlations and estimations have been made by using chemical shift data for solid compounds, there are both experimental and theoretical reasons for preferring the study of gaseous compounds. For example, by use of gaseous mixtures, it is a simple matter to measure chemical shifts between compounds of the same element from a single spectrum. Chemical shifts for gaseous compounds do not suffer from uncertainties of work functions which arise in the case of solid compounds.[4] Both theoretical and empirical calculations of core electron binding energies are much simpler for gaseous molecules than for solid compounds.

Experimental

Photoionization was accomplished with magnesium K_αX-radiation (1253.6 eV). An iron-free double-focusing magnetic spectrometer[16] was used to determine the kinetic energies of the photoelectrons. The

gases were introduced from a metal vacuum line into a 200-ml source chamber. During each run, the pressure within this chamber was held constant (to ± 20%) in the range 10-40 microns. First the pure compound was studied in order to determine the approximate magnitude of the photoelectron kinetic energy. Then an approximately one-to-one mixture of the compound and some convenient reference compound was studied. Nitrogen gas was the first choice as a reference because of its low reactivity, but other gases were used when the chemical shift was less than 2 eV from that of nitrogen gas. The width of each channel in the spectrum was 0.27 eV; the counting times were such that at least 1000 counts were recorded in the channel nearest the signal peak. The signal-to-noise ratios were in the range 4.0-8.7, and the widths of the photoelectron lines at half-height were in the range 1.0-1.5 eV. Most samples were run twice; we never observed a significant change in the chemical shift in different runs of the same compound. The spectrometer pressure was maintained at less than 10^{-4} microns.

Most of the gases were taken from commercial cylinders. Except for N_2, NO, N_2O and NF_3, samples were purified by vacuum distillation. The purity of each sample was checked by mass spectrometry and by comparison of the infrared spectrum with the literature.[17] Hydrogen cyanide was prepared by the addition of potassium cyanide to phosphoric acid in a closed system. Its mass and infrared spectra agreed with the literature.[17] Dr. William Fox of Allied Chemical Company kindly provided us with a sample of ONF_3.

Results and Discussion

The measured nitrogen 1s binding energies, relative to molecular nitrogen, are given in Table I. The values span a total range of 12.3 eV. In the following paragraphs we discuss these values in terms of the various methods of estimating chemical shifts in binding energies.

Atomic Charge Method. - Previous studies of the relation between binding energy and calculated atomic charge have shown only modest improvements in the correlations when more sophisticated methods for calculating atomic charge were used.[5-8] Consequently in this study we have used probably the simplest method for calculating charges, i.e. the Pauling method, based on the relation between the ionic character of a bond and the difference in the electronegativities of the atoms.[18] Pauling's method[19] for estimating the electronegativity of charged atoms was used, and the calculations were iterated until consistent sets of charges and electronegativities were obtained. For NO and NO_2, Linnett structures were used to establish the initial formal charges.[20] For N_2O, we used the average charges calculated from the initial structures $\bar{N}=\overset{+}{N}=O$ and $N\equiv\overset{+}{N}-O^-$. The calculated charges are listed in the third column of Table I, and Figure 1 is a plot of binding energy vs calculated charge. The least-squares fitted straight line, $E_B = 7.45\ q - 0.87$, fits the points poorly, with an average error of ± 1.62 eV.

Thermodynamic Method. - The difference in the nitrogen 1s binding energies of NH_3 and N_2 is the energy of the following reaction.

Table I. Nitrogen 1s Binding Energies for Some Gaseous Compounds

No.	Molecule	Relative Binding Energy, eV	Calculated Atomic Charge	Thermo. Estimated Rel. Binding Energy, eV
1	ONF_3	7.1	1.24	
2	NF_3	4.3	0.45	
3	NO_2	3.0 [a]	0.53	3.3[c,d]
4	$N\overset{*}{N}O$	2.6 [a]	0.51	
5	N_2F_4	2.4	0.32	2.8[d,e,f]
6	ONCl	1.5	0.05	
7	NO	0.8[a,b]	-0.37	0.9[c,d]
8	N_2	0.0	0.00	0.0
9	$\overset{*}{N}NO$	-1.3 [a]	-0.34	-0.9[c,d]
10	HCN	-3.1	-0.06	-2.6[c,d,g]
11	N_2H_4	-3.8	-0.26	
12	NH_3	-4.3 [a]	-0.39	-3.5[c,d,h,i]
13	CH_3NH_2	-4.8	-0.32	-3.9[c,d,i]
14	$(CH_3)_2NH$	-5.0	-0.23	-4.2[c,d,j]
15	$(CH_3)_3N$	-5.2	-0.15	

[a]The following values were obtained by Siegbahn et al (Ref. 9): NO_2, 2.99; $N\overset{*}{N}O$, 2.6; NO, 0.4; $\overset{*}{N}NO$, -1.4; NH_3, -4.3.

[b]Weighted average of two peaks caused by spin of molecule.

[c]U.S. National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D.C., 1952.

[d]National Standard Reference Data System, U.S. National Bureau of Standards, Washington, D.C., NSRDS-NBS 26, June 1969.

Table I. (Cont.)

[e]A. Kennedy and C. B. Colburn, J. Chem. Phys., 35, 1892 (1961).

[f]Calculated for the reaction $NF_2 + NO^+ \rightarrow OF_2^+ + N_2$. In view of the low dissociation energy of N_2F_4, this approximation is reasonable.

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[j]The proton affinity of $(CH_3)_2O$ was estimated to be 190 kcal/mole on the basis of data given by M. S. B. Munson, J. Am. Chem. Soc., 87, 2332 (1965).

$$NH_3 + N_2^{+*} \rightarrow NH_3^{+*} + N_2$$
$$\Delta E = E_B(NH_3) - E_B(N_2) \qquad (1)$$

(The asterisks indicate 1s electron vacancies.) If we make the approximation that $\Delta E = 0$ for any process in which an N^{6+} core in one species is interchanged with an O^{6+} core in another species, we may write

$$NH_3^{+*} + NO^+ \rightarrow OH_3^+ + N_2^{+*}$$
$$\Delta E = 0 \qquad (2)$$

Then, by adding reactions 1 and 2, we obtain

$$NH_3 + NO^+ \rightarrow OH_3^+ + N_2$$
$$\Delta E = E_B(NH_3) - E_B(N_2) \qquad (3)$$

Thus the shift in binding energy is, to the accuracy of our

approximation, equal to the energy of equation 3 - a quantity which can be evaluated from available thermodynamic data. Similarly, most of the other chemical shifts in Table I can be approximated by thermodynamic data. The thermodynamically estimated chemical shifts are listed in the fourth column of Table I. The average discrepancy between the experimental and estimated values is ± 0.52 eV. Figure 2 is a plot of the experimental binding energy shifts vs the estimated shifts.

Empirical Parameter Method. - It has been shown that chemical shifts in binding energy can be approximated by the sum of empirically-evaluated parameters characteristic of the attached atoms or groups.[11] This additivity rule can be checked with a few of the binding energy data in Table I.

When all three hydrogen atoms of ammonia are replaced with methyl groups, the binding energy decreases by 0.9 eV. In the case of monomethylamine, the decrease would be expected to be one-third as much, 0.3 eV, whereas it is actually 0.4 eV. In the case of dimethylamine the predicted and actual decreases are 0.6 and 0.7 eV, respectively.

The addition of an oxygen atom to the nitrogen atom of NF_3 causes the binding energy to increase by 2.8 eV. (This is the chemical shift between NF_3 and ONF_3.) A similar change would be expected on adding an oxygen atom to molecular nitrogen. Indeed, the binding energy for the middle atom of N_2O is 2.6 eV greater than that of the atoms in N_2.

The binding energy of NF_3 is 8.70 eV greater than that of NH_3. We would expect the difference between N_2F_4 and N_2H_4

to be a little more than two-thirds as great, i.e., a little greater than 5.80 eV. Indeed, the observed chemical shift between N_2F_4 and N_2H_4, 6.24 eV, is in agreement with this expectation. From the few comparisons made above, we tentatively conclude that the empirical parameter method is capable of predicting chemical shifts to about ± 0.2 eV.

Computational Method. - Basch and Snyder[13] have obtained nitrogen 1s orbital energies for some of the compounds in Table I from SCF-MO calculations using a double-zeta basis of gaussian functions. According to Koopmans' theorem, these energies may be taken as equal to binding energies. Their calculated values, relative to N_2, are (in eV): $N\overset{*}{N}O$ (3.9), $\overset{*}{N}NO$ (0.7), HCN (-2.4), N_2H_4 (-3.8), and NH_3 (-5.4). The average deviation of these values from the experimental values is ± 1.0 eV.

Conclusions

The Pauling atomic charge method, although it gives very rough correlations with binding energy, has the advantage that it can be applied to any set of molecules for which complete octet structures can be written. In the case of resonating molecules, ambiguity arises as to the relative weights of the resonance structures.[21] In these cases the experimental data can be used to establish the relative weights. Barber and Clark[15] cite the essentially equal carbon 1s binding energies of acetonitrile as evidence for the inadequacy of atomic charge-binding energy correlations. It is true, that by use of only the $H_3C-C{\equiv}N$ structure, the CN carbon atom would be expected to have

a significantly greater binding energy than the CH_3 carbon atom.[22] However contribution from the hyperconjugated $H^+H_2C{=}C{=}N^-$ structure (which cannot be ignored, in view of the observed acidity[23] of acetonitrile) would bring the carbon atom charges closer together, and the binding energy data may be taken as further evidence for such hyperconjugation.

The thermodynamic method gives more accurate predictions than the atomic charge method, and it is completely nonempirical, at least with respect to binding energies. However it is applicable only when the appropriate heats of formation are known or can be estimated.

The empirical parameter method has not yet been adequately tested with accurate gas-phase binding energy data. However, the few comparisons which we have been able to make indicate that, with the availability of appropriate sets of empirical data, the method should yield very accurate predictions.

Relatively few comparisons have been made between experimental and highly refined molecular orbital-calculated binding energies. The available results show agreement to ± 1 eV and suggest that the error due to the assumption of Koopmans' theorem is approximately the same for all molecules.[14]

Acknowledgement: This work was performed under the auspices of the U. S. Atomic Energy Commission.

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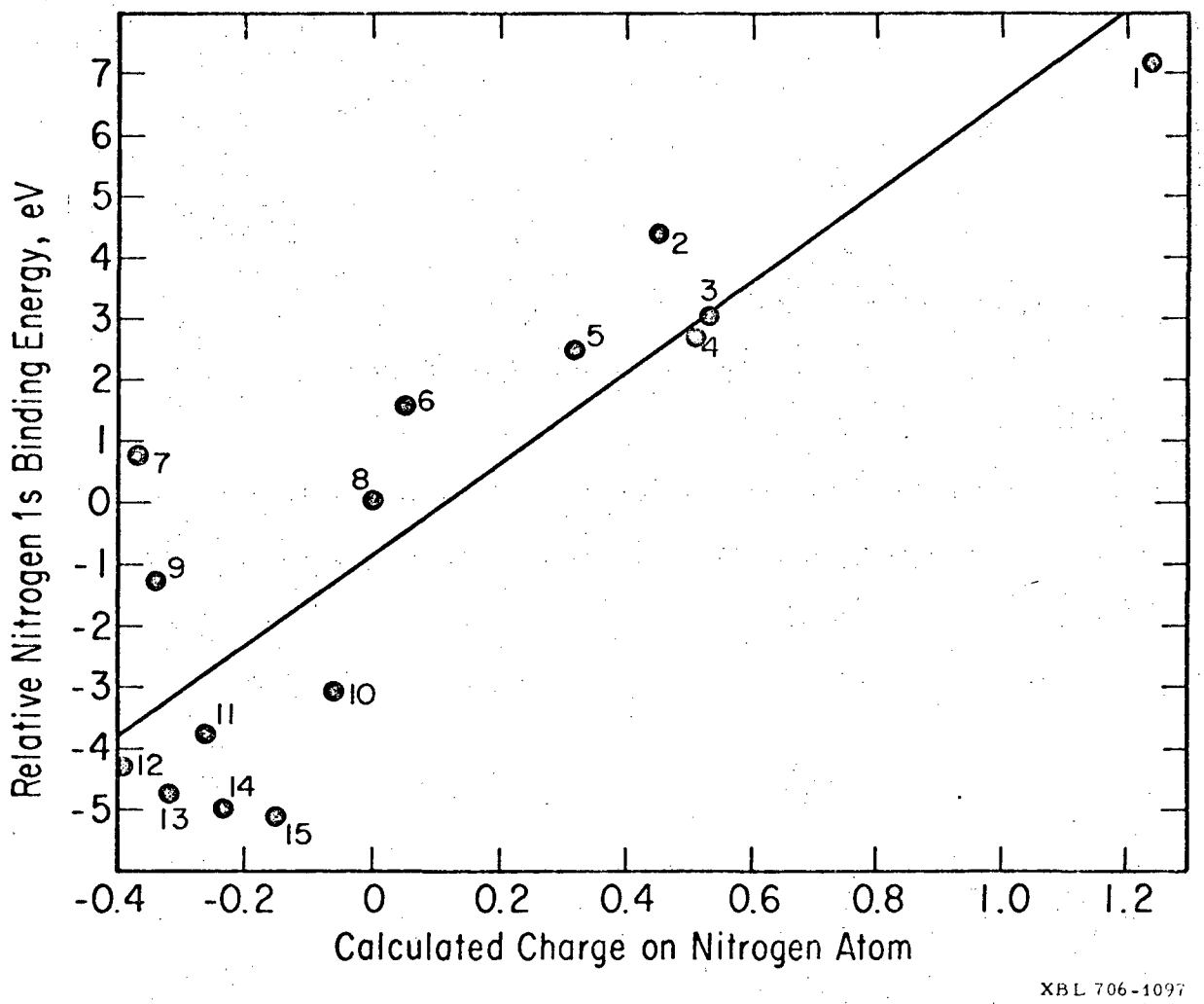

Figure 1. Correlation of binding energy with atomic charge calculated by the Pauling method. Numbers refer to the compounds in Table I.

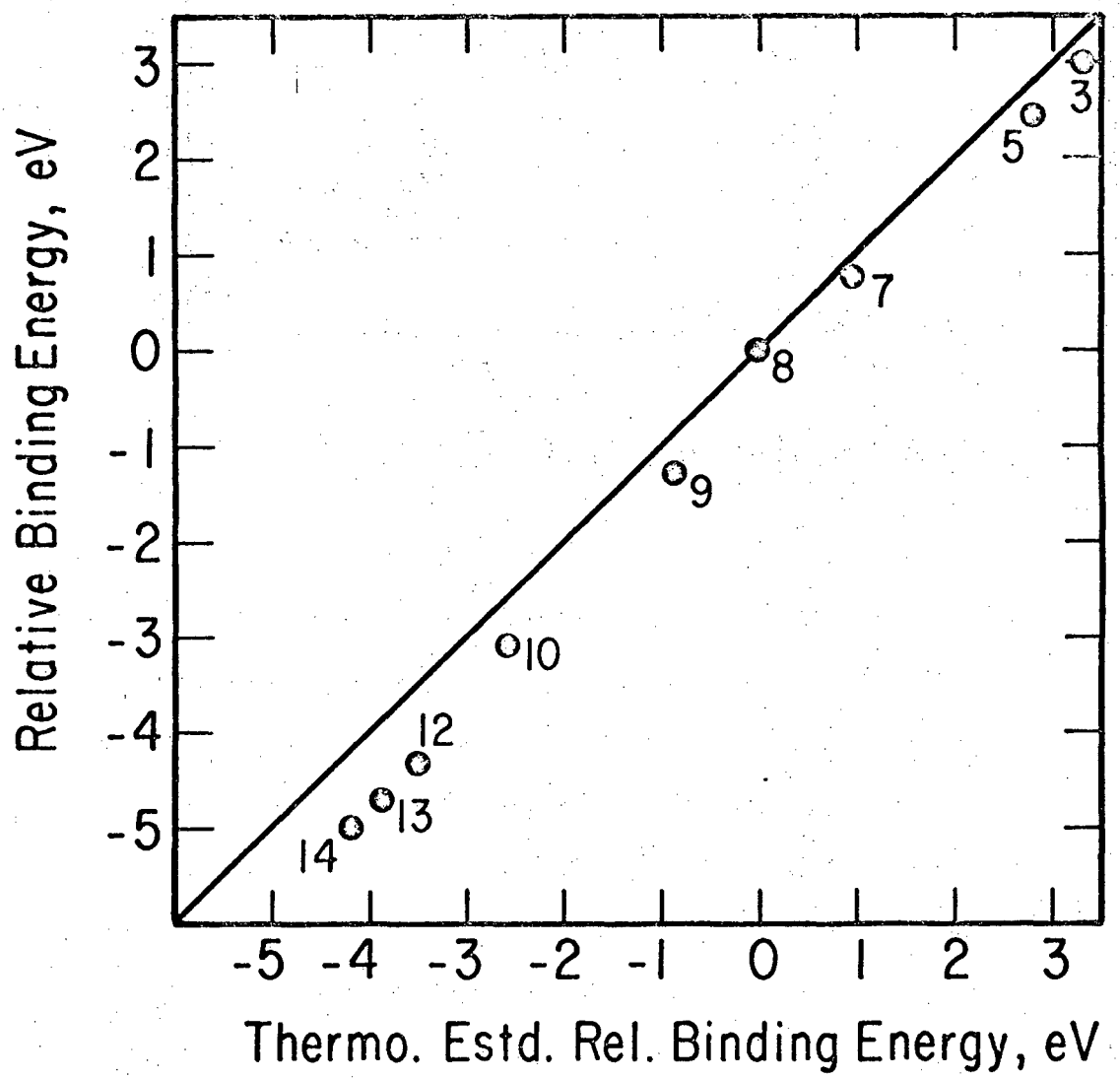

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Figure 2. Comparison of experimental and thermodynamically estimated binding energies. The line has a slope of unity and passes through the origin. The numbers refer to the compounds in Table I. The line would fit the points much more closely if point 9 or 10 (rather than 8) had been arbitrarily placed at the origin. It is significant that most of the points fit a line of unit slope.

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