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THE CORRELATION OF CORE REPLACEMENT
ENERGIES WITH NONBONDING s ELECTRON
DENSITY

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ABSTRACT:

Core replacement energies are calculated for nitrogen and oxygen in various gaseous cations from accurate core binding energies and thermodynamic data. The values for a given element differ in some cases by much more than the experimental errors. These chemical shifts in core replacement energy can be rationalized by recognizing that they are equal to the shifts in the energy of transferring an electron from a core level to a nucleus. As expected, relatively endothermic core replacement energies are found for atoms which have a high density of nonbonding valence s electrons.

The equivalent cores approximation was first used in X-ray photoelectron spectroscopy to predict chemical shifts in core electron binding energies [1-3]. This and many subsequent applications of the approximation have recently been reviewed [4]. The essence of the approximation may be expressed as follows: The energy of the process in which an electron is transferred from a core level of an atom to the nucleus of the atom is independent of the chemical environment of the atom. In the case of an ion $M(Z)^+$ containing an atom of atomic number Z , this process may be represented thus:

The asterisk is used to indicate a core vacancy. Although eq. (1) is balanced with respect to electrons, protons, and neutrons (assuming the elements of atomic number Z and $Z-1$ have the same mass number), it is not balanced with respect to the elements involved, as in a normal chemical reaction. However we can convert it into a balanced chemical reaction, and change its energy by a constant amount, by the appropriate addition of the species corresponding to the elements of atomic number Z and $Z-1$ in their standard states.

According to the equivalent cores approximation, the energy of reaction (2) is the same for all ions $M(Z)^+$; we shall refer to the energy of this reaction as the core replacement energy, and shall give it the symbol Δ_Z .

The core ionization of a molecule $M(Z-1)$ has an energy equal to the

binding energy of the core electron, $E_B[M(Z - 1)]$, and is represented by the following equation.

If we subtract eq. (3) from eq. (2), we obtain eq. (4), which has an energy $E_B[M(Z - 1)] + \Delta_Z$.

It should be noted that eq. (4) is a normal chemical reaction involving no core-ionized species. In principle, the energy (or heat) of reaction (4) can be obtained from thermochemical measurements, and we can write

$$\Delta_Z - E_B[M(Z - 1)] = \Delta H_f^\circ[M(Z - 1)] - \Delta H_f^\circ[M(Z)^+]$$

(Note that, by definition, the heats of formation of the elements in their standard states and the gaseous electron are zero.) Obviously the core replacement energy can be calculated from a binding energy and appropriate thermodynamic data. Thus the core replacement energy Δ_N can be calculated from the C 1s binding energy for methane and the heats of formation of NH_4^+ and CH_4 :

$$\begin{aligned} \text{C}_{\text{graphite}} + \text{NH}_4^+ &\longrightarrow \frac{1}{2}\text{N}_2 + \text{CH}_4^{*+} \\ \Delta_N &= E_B(\text{CH}_4) + \Delta H_f^\circ(\text{CH}_4) - \Delta H_f^\circ(\text{NH}_4^+) \\ &= 290.88 - 0.78 - 6.61 \\ &= 283.49 \text{ eV} \end{aligned}$$

Elsewhere [5,6] the term "core exchange energy," δ , has been applied to processes such as the following.

We believe the use of the elements in their standard states, rather than the cores, has two advantages: (1) Values of Δ_Z can be more accurately determined than the corresponding values of δ . (For example, the energy of formation of P^{5+} is uncertain by about ± 10 kcal/mol because of uncertainty in the heat of formation of gaseous P atoms.) (2) The Δ_Z values can be more conveniently used in numerical calculations because it is unnecessary to involve the heats of formation of the core ions.

Values of Δ_N calculated from data for 9 different nitrogen-containing cations and the isoelectronic carbon compounds (including $\text{NH}_4^+/\text{CH}_4$) are given in Table 1. The first 8 values are very close to their average value, 283.68 eV (average deviation ± 0.17 eV, standard deviation 0.21 eV). The last value, calculated from data for NO^+ and carbon monoxide, is 1.22 eV greater than the average of the other values. There is no reason to doubt the accuracy of any of the quantities involved in calculating Δ_N for NO^+/CO , and we believe the large difference is real. We conclude that Δ_Z is not exactly constant for all compounds of a given element and that it can shift by amounts considerably greater than experimental error. The question is, what sort of chemical information can be obtained from the observed shifts in core replacement energy?

The core replacement reaction, involving the transfer of an electron from a core to a nucleus, should not change much on going from one compound to another as long as the differences in electron density of the atom in question are mainly outside the region of the core. However if the atom has

Table 1.

Core replacement energies for nitrogen-containing cations.

Compounds	$E_B(\text{C } 1s)$, eV	E_B Ref.	Δ_N , eV	ΔH_f° Ref.
$\text{NHF}_3^+/\text{CHF}_3$	299.1	[7]	283.9	[8-10]
$\text{NO}_2^+/\text{CO}_2$	297.71	[11]	283.69	[12,13]
HN_2^+/HCN	293.5	[14]	283.9	[12,15]
$\text{HCNH}^+/\text{C}_2\text{H}_2$	291.14	[16]	283.86	[12,17]
$\text{NH}_4^+/\text{CH}_4$	290.88 ^{a)}	[18]	283.49	[12,19,20]
$\text{CH}_3\text{NH}_3^+/\text{C}_2\text{H}_6$	290.74 ^{a)}	[18]	283.39	[12,20]
$\text{C}_5\text{H}_5\text{NH}^+/\text{C}_6\text{H}_6$	290.42	[21]	283.46	[12,19]
$\text{CH}_3\text{CNH}^+/\text{CH}_3\text{CCH}$	290.40	[16]	283.71	[12,17,22]
NO^+/CO	296.24	[23]	284.90	[12]

a) The value differs from that in ref. [18] because of a spectrometer recalibration and the use of 248.62 eV as the Ar $2p_{3/2}$ reference.

a relatively high electron density at the nucleus (because, for example, of nonbonding valence electrons with considerable s character), the core replacement energy will be relatively endothermic - i.e., more positive. On this basis we can explain the very high Δ_N for NO^+/CO . The nitrogen atom of NO^+ differs from those of the other nitrogen cations in that it has a nonbonding pair of valence electrons. Nonbonding electrons generally have a much higher fraction of s character than bonding electrons; hence the nitrogen atom of NO^+ has an abnormally high electron density at its nucleus. Of course, the carbon atom of carbon monoxide also has an abnormally high s electron density.

In order to test the preceding explanation for chemical shifts in core replacement energy it would be useful to have Δ_N values for other cations containing nitrogen atoms with lone pair electrons. Unfortunately there are no experimental data for calculating such Δ_N values. Therefore we have calculated core exchange energies, δ_C (see reaction 5), for the hypothetical ion/molecule pairs HN_2^+/HNC , $\text{H}_2\text{NNH}^+/\text{H}_2\text{NCH}$, and $\text{H}_3\text{NNH}_2^+/\text{H}_3\text{NCH}_2$ by an ab initio LCAO MO SCF method and have converted these to Δ_N values using the known heats of formation N^{5+} and C^{5+} [12,24]. The ATMOL 2 group of programs, with a basis set of optimized Gaussian functions consisting of 4s contracted to 3s for H and 9s, 5p contracted to 5s, 3p for C and N, was used for the calculations [25,26]. The bond angles for HN_2^+/HNC , $\text{H}_2\text{NNH}^+/\text{H}_2\text{NCH}$, and $\text{H}_3\text{NNH}_2^+/\text{H}_3\text{NCH}_2$ were taken to be 180° , 120° , and 109.47° , respectively, and an initial bond distance optimization was performed using a 4.31G basis set. Full details of the basis sets used and the calculational procedure have been described [5]. In table 2 are listed the δ_C and Δ_N values for the hypothetical species and the Mulliken 2s populations of the nitrogen valence lone pairs of the cations. Some

Table 2.

Calculated values of core replacement energy for nitrogen-containing cations

Compounds	δ_C , eV	Δ_N , eV	N 2s population of N valence lone pair
NO^+/CO	-9.4 ^{a)}	285.1	0.605
HN_2^+/HNC	-9.15	284.82	0.893
$\text{H}_2\text{NNH}^+/\text{H}_2\text{NCH}$	-8.52	284.19	0.206
$\text{H}_3\text{NNH}_2^+/\text{H}_3\text{NCH}_2$	-8.04	283.71	0.149
$\text{NO}_2^+/\text{CO}_2$	-8.4 ^{a)}	284.1	
$\text{NH}_3\text{F}^+/\text{CH}_3\text{F}$	-7.8 ^{a)}	283.5	

a) From ref. [5] using the corresponding basis set.

previously calculated data for "normal" compounds are also included. The data clearly show that the nitrogen core replacement energy becomes more endothermic as the nonbonding s electron density on the nitrogen atom increases.

The effect of the s character of nonbonding electrons on core replacement energy can be seen in the data for oxygen-containing cations, shown in Table 3. We have separated the compounds into two groups. The first group consists of compounds in which the nonbonding electrons on the oxygen atom would be expected to have a relatively high fraction of s character, and the second group consists of compounds expected to have relatively low s character in the oxygen nonbonding electrons. The first group contains oxygen atoms bonded to just one other atom (in which the nonbonding electrons can be roughly described as having sp hybrid character) or, in the case of OF_2^+ , bonded to two extremely electronegative atoms which principally involve the p orbitals of the oxygen atom in bonding. The second group contains trivalent oxygen atoms (in which the nonbonding electrons can be roughly described as having sp^3 hybrid character) and, in the case of O_3^+ , an oxygen atom containing only one nonbonding electron having approximately sp^2 hybrid character. The average Δ_0 value for the first group is 399.63 eV (ave. dev. ± 0.18 eV, std. dev. 0.29 eV), and that for the second is 399.04 (ave. dev. ± 0.18 , std. dev. 0.24). The difference of 0.59 between the average Δ_0 values for the two groups is in the expected direction and has a magnitude considerably greater than could be explained by experimental error.

Thus several sets of data have shown that core replacement energies can be used as indicators of electron density at nuclei and, in the case of atoms with nonbonding valence s electrons, can give information about

Table 3.

Core replacement energies for oxygen-containing cations.

Compounds	$E_B(\text{N } 1s)$, eV	E_B Ref.	ΔO , eV	ΔH_f° Ref.
$\text{OF}_2^+/\text{NF}_2$	413.0	[24]	400.0	[12]
O_2^+/NO	410.6	[28,29]	399.5	[12]
NO^+/N_2	409.95	[30]	399.75	[12]
$\text{NO}_2^+/\text{NNO}^*$	408.5	[31]	399.4	[12,13]
HCO^+/HCN	406.8	[28]	399.7	[12,32]
$\text{CH}_3\text{CO}^+/\text{CH}_3\text{CN}$	405.41	[33]	399.73	[12]
$\text{CH}_2\text{CHCO}^+/\text{CH}_2\text{CHCN}$	405.28	[33]	398.97 ^{a)}	[12]
O_3^+/NO_2	412.9	[27,28]	399.4	[12]
$\text{OH}_3^+/\text{NH}_3$	405.60 ^{b)}	[34]	398.88	[12,35]
$\text{CH}_3\text{OH}_2^+/\text{CH}_3\text{NH}_2$	405.2	[28]	399.0	[12,36,37]
$(\text{CH}_3)_2\text{OH}^+/\text{(CH}_3)_2\text{NH}$	405.0	[28]	398.9	[12,36,37]

a) Because of uncertainty in ΔH_f° for $\text{C}_3\text{H}_3\text{O}^+$, this value has been weighted only one-half as much as the other values.

b) The value differs from that in ref. [34] because of the use of 248.62 eV as the Ar $2p_{3/2}$ reference.

the hybridization of the atomic orbitals.

The transfer of an electron from a $1s$ level to a nucleus is the well known process of K electron capture, and so on the basis of our results one expects chemical shifts in the measured energies of spontaneous K electron capture. Unfortunately at present there is no good way for accurately measuring such chemical shifts. Of course, the rate constant for electron capture is directly proportional to the electron density at the nucleus, and electron capture half-lives have been observed to be dependent on chemical environment [38]. Mössbauer isomer shifts are sensitive to changes in electron density at nuclei and yield information similar to that obtainable from core replacement energy shifts [39]. Because core replacement energy shifts can in principle be measured for any element heavier than helium, they have a much wider potential applicability than Mössbauer isomer shifts.

Core replacement energy shifts are closely related to the differences between shake-up excitation energies and the corresponding electronic excitation energies of isoelectronic cations. If an electronic transition causes the nonbonding electron density on a particular atom to increase, the shake-up excitation energy obtained from the core spectrum of that atom should be greater than the normal electronic excitation energy of the isoelectronic cation in which the atom has been replaced with an atom of the next element in the periodic table. For example, the $2p\pi^b 1\Sigma^+$ to $2p\pi^* 1\Sigma^+$ N $1s$ shake-up excitation energy of N_2 should be greater than the normal excitation energy of NO^+ (which, according to Edqvist et al. [40], has a value around 12.5 eV). Unfortunately the assignment of shake-up satellites, even for molecules as simple as N_2 , is still argumentative [41]. However it is significant that the most intense

shake-up peak of N_2 has an excitation energy of 16.0 eV [42].

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