# A study of correlation of the order of chemical reactivity of a sequence of binary compounds of nitrogen and oxygen in terms of frontier orbital theory

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The order of stability and chemical reactivity of a sequence of nine compounds of nitrogen and oxygen have been correlated in terms of the energies of the frontier orbitals. The order of stability has been correlated in terms of the height of the energy gap between the highest occupied molecular orbital and lowest occupied molecular orbital and the global hardness of the molecules while the order of chemical reactivity has been correlated in terms of their global softness.

NITROGEN and oxygen form a number of binary combination products called oxides of nitrogen and as many as nine such oxides, viz. N_2O, N_2O_3, N_2O_4, N_2O_5, NO_3^-, NO_2^-, NO^-, NO_2^+ and NO^+ are known. The compounds are widely divergent in thermodynamic stability and chemical reactivity. Text books usually draw and discuss the electronic structure of such molecules invoking qualitative LCAO-MO theory, valence bond theory and the theory of n-center bonding. The electronic structures drawn in terms of such theories of bonding and chemical reactivities of such molecules are shown in Table 1. From a careful study of the electronic structures and chemical response of the molecules from the available source materials[1-7], the molecules can be arranged in a sequence of increasing or decreasing order of thermodynamic stabilities and chemical reactivities. The chemical reactivity order or the order of response of the molecules towards attacking reagents may be arranged as follows:

$$NO^+ < NO_3^- < NO_2^+ < NO_2^- < NO^- < N_2O_5 < N_2O$$
$$< N_2O_4 < N_2O_3 : \text{order of chemical response.}$$
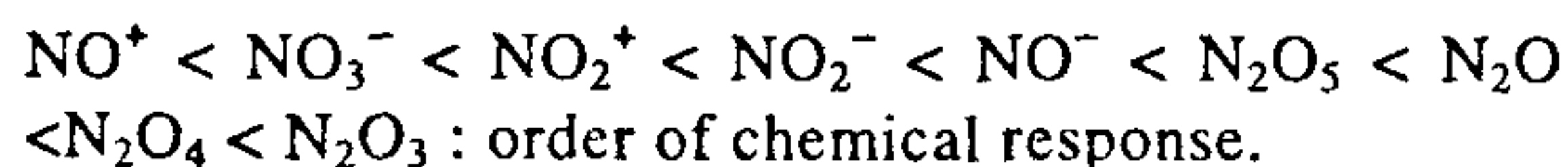
The order of thermodynamic stabilities of the molecules is just the reverse of the above sequence.

$$N_2O_3 < N_2O_4 < N_2O < N_2O_5 < NO^- < NO_2^- < NO_2^+$$
$$< NO_3^- < NO^+: \text{order of thermodynamic stability.}$$
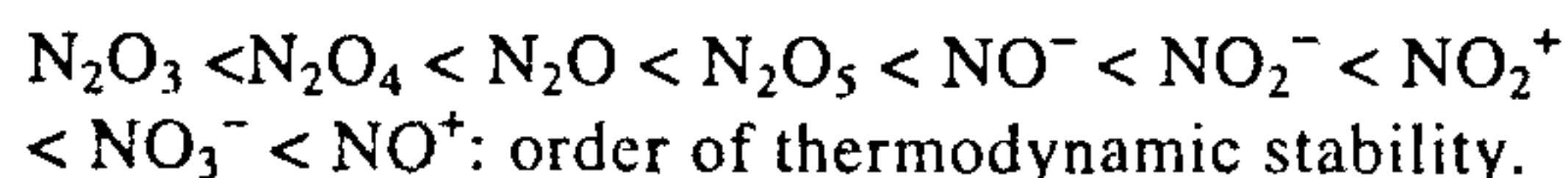
The intrinsic chemical reactivity or inertness and the inherent thermodynamic stability of molecules are not straightforward and evident in terms of electronic structures drawn in terms of the above mentioned theories of bonding as shown in Table 1. The relative ther-

modynamic stabilities and chemical response of different molecules are hardly intelligible in terms of such electronic structures.

But a study of the energies and symmetry types of a pair of frontier orbitals of molecules, within the framework of Self-Consistent Field Molecular Orbital Theory[8], may furnish reliable and quantitative data for a straightforward prediction and comparative study of chemical and thermodynamic stabilities of molecules.

The highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO, of a molecule are called the frontier orbitals. It was Fukui[9] who first noticed the prominent role played by HOMO and LUMO in governing chemical reactions. It has been revealed by recent investigation that the gap in energy between the HOMO and LUMO is an important stability index[10-12]. A large gap implies high stability and small gap implies low stability. The high stability in turn indicates low chemical reactivity and small gap indicates high chemical reactivity. The energy and symmetry type of, and the charge distribution in HOMO, and the energy and symmetry type of LUMO are known to determine the structures[13-15] of molecules. The energy and symmetry types of such frontier orbitals are also found to be the principal factor for determining the occurrence and non-occurrence of chemical reactions and stereo-selective path in intra- and inter-molecular processes[16].

Another very useful theory of electronic structure and reactivity of molecules involving the single pair of frontier orbitals is the Hard–Soft Acid Base (HSAB) principle of Pearson[17]. The work of Parr, Pearson and others[11,18-26], within the framework of Density Functional Theory (DFT), has established a general rule predicting the stability of the electronic structure of molecules. The general rule of this new paradigm is that the index of chemical reactivity and stability of a molecule is its global hardness, η. Increase in hardness increases the movement of the system towards a more stable configuration and when a chemical species moves away from its equilibrium configuration its hardness value decreases. When a system evolves towards a state of greater hardness, its stability increases. When a system evolves towards the state of lower hardness, its stability decreases. η, is again used as an index of chemical reactivity. The higher the value of η, the lesser is its reactivity. The global softness, S, the inverse concept of hardness, is useful for a straightforward prediction of chemical reactivity. The soft molecules undergo changes in electron density more easily than the hard molecules and are more reactive than the hard molecules. A molecule having higher S value is more reactive than a molecule having smaller S value. In general, it can be said that the increase in softness increases chemical reactivity and increase in hardness decreases chemical reactivity.

Table 1. Formula, name, electronic structure and properties of binary compounds of nitrogen and oxygen

| Formula	Name	Electronic structure	Remark
N_2O	Nitrous oxide	linear, $C_{\infty v}$	Not very reactive
N_2O_3	Dinitrogen trioxide	planar, Cs	Extensively dissociated as gas
N_2O_4	Dinitrogen tetroxide	planar, D_{2h}	Forms colourless liquid and in equilibrium with NO_2 in gas phase
N_2O_5	Dinitrogen pentoxide	planar, C_{2v}	Colourless ionic solid, unstable in gas phase
NO_2^-	Nitrite	C_{2v}	Weak base, oxidizing and reducing agent
NO_3^-	Nitrate	planar, D_{3h}	Very weak base, oxidizing agent
NO^-	Nitric oxide anion	$C_{\infty v}$	Shows Lewis basicity
NO^+	Nitrosonium	$C_{\infty v}$	Lewis acid and oxidizing agent
NO_2^+	Nitronium	linear, $D_{\infty h}$	Oxidizing agent, nitrating agent and Lewis acid

It is, therefore, quite evident that the quantum chemical quantities – the HOMO–LUMO gap, the global hardness and the global softness can be used for a quantitative prediction of intrinsic stability, chemical reactivity as well as the relative stabilities and chemical reactivities of molecules. By comparative analysis of the computed values of $\Delta\varepsilon$, η and S of a series of molecules, one can arrange the molecules in a sequence of increasing or decreasing order of chemical reactivity and thermodynamic stability. The global hardness and the global softness are conventionally computed through frontier orbitals with the help of Koopmans' theorem[27]. The $\Delta\varepsilon$ is simply obtained from the energies of the frontier orbitals.

The symmetry types and the energies of the frontier orbitals of each of the molecules are computed at their experimental geometry by invoking the CNDO/2 level Self-Consistent Field Molecular Orbital method of Pople[28] and co-workers. The STO basis set and standard parameters are used in this calculation. The desired

Table 2. Symmetry types. energies, height of gap between energies of the HOMO and LUMO global hardness and global softness of the molecules

| Chemical systems | HOMO | | LUMO | | $\varepsilon_{LUMO} - \varepsilon_{HOMO}$ $(\Delta\varepsilon)$ a.u. | Global hardness (η) a.u. | Global softness (S) a.u.$^{-1}$ |
	Symmetry type	Energy (ε_{HOMO}) a.u.	Symmetry type	Energy (ε_{LUMO}) a.u.			
NO^+	σ^+	−1.3579	π	−0.4178	0.9401	0.4700	2.1276
NO_3^-	e'	−0.1961	a_2''	0.4754	0.6715	0.3357	2.9788
NO_2^+	σ^+_u	−1.0658	σ_u^+	−0.4062	0.6596	0.3298	3.0321
NO_2^-	a_1	−0.0703	a_1	0.5519	0.6222	0.3111	3.2144
NO^-	σ^+	0.0881	σ^+	0.6817	0.5936	0.2968	3.3693
N_2O_5	a_1	−0.5074	a_1	0.0167	0.5241	0.2620	3.8168
N_2O	π	−0.5099	σ^+	−0.0544	0.4555	0.2277	4.3917
N_2O_4	b_{1u}	−0.4643	b_{1u}	−0.0201	0.4441	0.2220	4.5045
N_2O_3	a''	−0.4302	a''	0.0054	0.4356	0.2178	4.5914
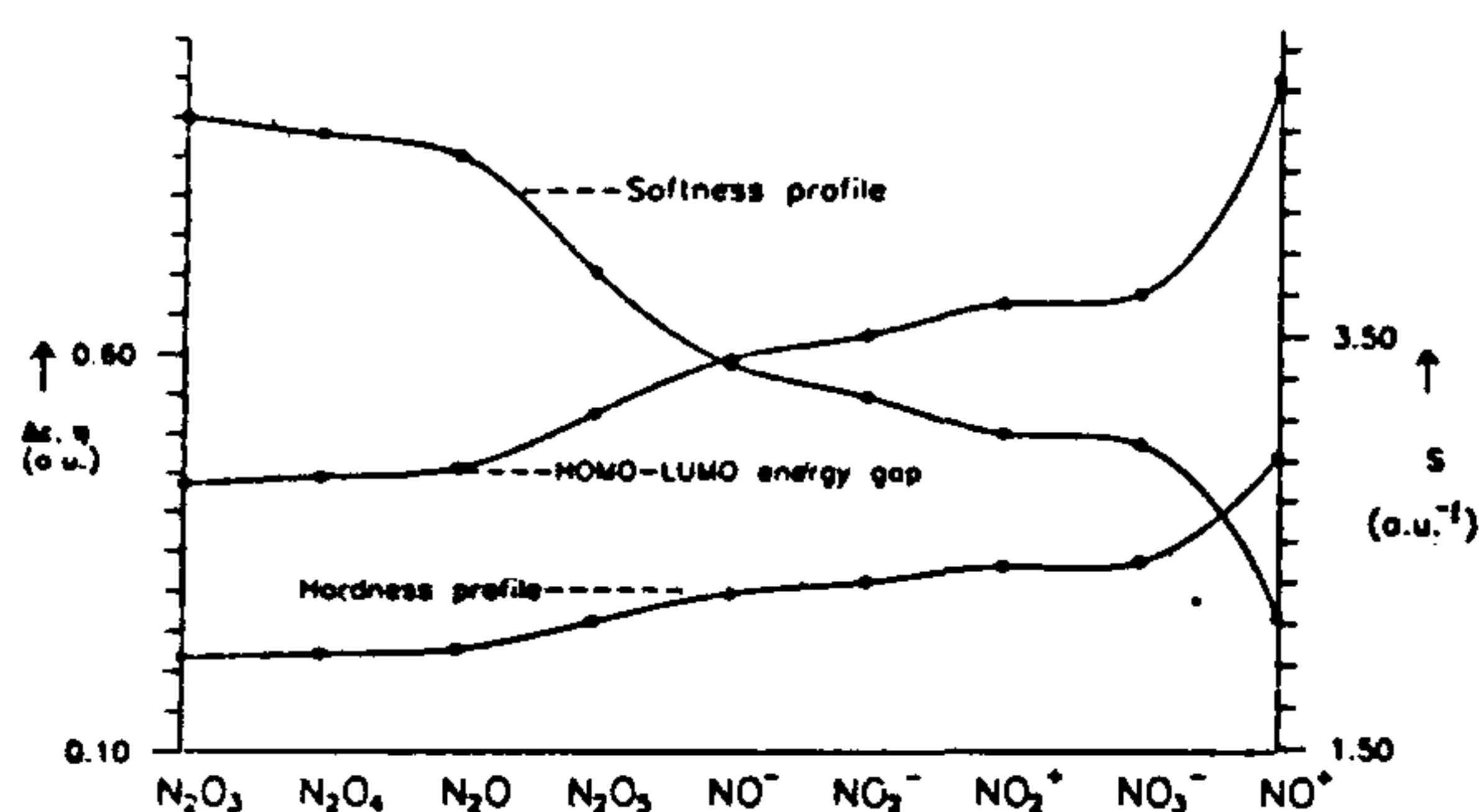
Figure 1. Plot of the energy gap between the HOMO and the LUMO, $\Delta\varepsilon$ (a.u.), the global hardness, η (a.u.) and global softness, S (a.u.$^{-1}$) of the molecular species.

quantities $\Delta\varepsilon$, η and S of each molecular system are then calculated using the computed energies of their frontier orbitals.

$$\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}, \qquad (1)$$

where $\Delta\varepsilon$ is the difference between the energies of LUMO and HOMO; ε_{LUMO} is the energy of the lowest unoccupied molecular orbitals, LUMO; and ε_{HOMO} is the energy of the highest occupied molecular orbitals, HOMO.

$$\eta = (\varepsilon_{LUMO} - \varepsilon_{HOMO})/2, \qquad (2)$$

where η is the global hardness.

$$S = 1/\eta, \qquad (3)$$

where S is the global softness.

$\Delta\varepsilon$, η are calculated in hartree unit and S in hartree^{-1} unit. The computed data of all the molecules are shown in Table 2 and plotted in Figure 1.

From Table 2 we see that the HOMO and LUMO of the nitrosonium cation, $(NO)^+$, are σ and π-type respectively and are highly stable. $\Delta\varepsilon$, the height of the gap between the energies of these frontier orbitals, is quite high. This high stability of the frontier orbitals and the

large energy gap between them show that the $(NO)^+$ system should not be easily susceptible to chemical attack and should be chemically inert. The computed value of global hardness of $(NO)^+$ is very high and is close to the hardest of the chemical systems[20] and the species is thermodynamically very stable. Although it forms nitrosyl complexes with transition metals and metal analogues, it functions as a very poor σ-donor but strong π-acceptor. A quantum chemical calculation[29] has established that $(NO)^+$ is a very poor Lewis base and the ratio of the amount of back-donation to donation of charge is 4:1. The poor Lewis basicity and reactivity of $(NO)^+$ is also demonstrated by a Localized Molecular Orbital calculation[30]. Thus the computed values of the present theoretical quantities correlate with the high thermodynamic stability and intrinsic chemical inertness of the $(NO)^+$ system. Comparing the $\Delta\varepsilon$, η and S of $(NO)^+$ with those of other molecules of the series, we see that $\Delta\varepsilon$ and η are maximum and S is minimum in the series. Thus, $(NO)^+$ is structurally the most stable and chemically the most non-responsive of the series of molecules. Thus the computed theoretical quantities determining the chemical reactivity and stability of the electronic structure of molecules not only reveal the chemical inertness of $(NO)^+$ but also justify its position at the bottom of the list of molecules arranged in increasing order of chemical reactivity and at the top of the sequence arranging molecules in the order of stability.

In the case of the N_2O_3 molecule which is extremely unstable and occurs at the top of the list while arranging the molecules in increasing order of reactivity, $\Delta\varepsilon$ is small, global softness is high and global hardness is close to the most unstable systems[20]. The computed values of $\Delta\varepsilon$, η, and S predict that N_2O_3 should be highly chemically sensitive, responsive, structurally unstable and fluxional. The experimental fact is that N_2O_3 is the most chemically reactive and unstable in the series of molecules. When compared with other systems, we find that $\Delta\varepsilon$ and η values of N_2O_3 are minimum and S value is maximum in the series. Thus, the present calculation

not only predicts the extreme instability and chemical reactivity of N_2O_3 but also justifies its position at the top of the series arranged in order of increasing chemical reactivity.

High resonance stability of NO_3^- explains the strong acidity of HNO_3 and weak basicity of NO_3^-. The present computed data show that NO_3^- should be structurally stable and unreactive. NO_2^+ is expected to be harder because of its positive charge than the negatively charged NO_3^-. But NO_2^+ is extensively used as a nitrating agent and is more reactive than NO_3^-. The computed values of $\Delta\varepsilon$ and S predict that NO_2^+ should be more chemically reactive than NO_3^-. The global hardness of NO_2^+ is smaller than that of NO_3^-. This suggests that NO_2^+, in spite of its positive charge, should be more reactive than NO_3^-. The well-known reactivity of NO_2^+ compared to that of NO_3^- is theoretically predicted in this calculation.

The computed values of $\Delta\varepsilon$, η and S of the remaining systems, e.g. NO_2^-, NO^-, N_2O_5, N_2O and N_2O_4 reveal that these molecules should be progressively unstable and chemically reactive. The magnitude of $\Delta\varepsilon$ predicts that none of the systems are expected to be highly stable. This is just a corroboration of experimental observations regarding these molecules.

The gradual variation in stability and chemical reactivity in the series of molecules is well represented in Figure 1. The hardness profile and the profile of $\Delta\varepsilon$, the energy gap between the frontier orbitals, increase monotonically starting with the most reactive and structurally unstable species and ending with the most structurally stable and chemically unreactive species. There is a sharp inflexion in the curve around the point of most stable system $(NO)^+$. A close look at the profile of $\Delta\varepsilon$ and η reveals that the N_2O_5, N_2O, N_2O_4 and N_2O_3 molecules cluster around the same region of the curve. This clustering suggests that the thermodynamic stability and chemical reactivity of these molecules should be very close. The computed data demonstrate that all such systems are unstable and reactive, although there is a small relative variation in the degree of chemical reactivity and stability. The softness profile also reveals the conditions of chemical reactivity and stability of these molecules noted experimentally. The most reactive species is the most soft molecule which occupies the highest position in the softness profile curve. The most stable and unreactive species occur at the lowest position and there is also an inflexion point near their point of occurrence in the curve. The other molecules appear between the most hard and the most soft of the series. The softness profile, like the hardness profile, is thus equally applicable to predict the conditions of chemical reactivity and stability and for a comparative study of such properties of molecules.

The very useful qualitative and quantitative concept of electronic structure and chemical reactivity – the quantum mechanical theory of hardness and softness, quantitatively predicts the conditions of intrinsic thermodynamic stability and chemical reactivity in each of the molecular species. The relative order of the stability and reactivity of the molecules can also be ascertained from the computed values of $\Delta\varepsilon$, η and S. The computed values of the energy gap between the pair of frontier orbitals, the global hardness and the global softness justify the sequence of thermodynamic stability and chemical reactivity order of the series of molecules formed by nitrogen and oxygen.

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