RESEARCH ARTICLE

Geometries, Reactivity and Binding Energy of Urea on Mg_9O_9

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Abstract:

In this paper we present global and local reactivity results of the urea gas phase molecule and gas phase $(MgO)_{18}$ cluster for understand charge distribution and binding energy (MgO)-urea. We analyze the quantum chemical descriptors, *ionization potential* (I), *electron affinity* (A), *chemical hardness* (η), *chemical potential* (μ) and *Global Philicity Index* (ω) and site reactivity or site selectivity condensed Fukui function analysis of the distribution of atomic charges investigated with methods of *Mulliken*, *Merz-Kolman* and *Natural Atomic Charges*. For example, the binding energies of the MgO-urea systems are calculated using the total energies of the ground states of the respective Mg_9O_9 clusters and the isolated urea molecules and of the urea-Mg_9O_9 systems. Hyperconjugative Interaction, Infra Read (IR), Vibrational Circular Dichroism (VCD) and Raman Spectrum were also studied for all systems.

Keywords: Urea, DFT, Reactivity, Binding Energy.

Introduction

The reaction capacity of the metal oxides is perhaps the most important property of these oxides and determined by their electronic structures. The presence of the oxygen ions in the structure of these crystals of the closed shell $2s^2 2p^6$ configuration, thereby making the oxygen ions formally O^{2-} (i.e., the "oxide" ion). The chemical concept of ionic charge is useful, however, the actual distribution of electron density in a crystalline structure is very complicated to fit perfectly into such a simple concept. MgO is a highly ionic metal oxides example whose charge density of electrons in the crystal resembles that of a set of Mg^{2+} and O^{2-} ions. It should be noted that the O^{2-} "free" ion does not exist, compared to the free O atom, unless it is stabilized by means of positively charged linkers.

Competing Interests: The author has declared that no competing interests exists.

When we take a MgO cluster system we see that the reactive capacity of its atoms varies with the location of the atoms in the corners, sides or surfaces. A study based on quantum chemistry in order to understand the reactive degree of these atomic sites are of fundamental importance linked to the catalytic processes for metallurgy, pharmaceuticals, catalytic processes in general. Defects and vacancies take part in these processes, in many cases, decisively. The spatial distribution of the two electrons associated with a neutral oxygen vacancy depends on the degree of covalence of the oxygen-cation bond and topological factors: the crystalline structure of the oxide and the coordination of the place of the wave. In some cases, as in the MgO, the electrons are trapped in the place of the wave by the strong electrostatic potential exerted by the neighboring cations, thus forming a surface center F. Oxide surfaces have great applications in advanced technologies such as corrosion protection, coating for thermal applications, in catalysis as inert supports or directly as catalysts, in microelectronics due to their dielectric properties. There are many technological applications of MgO[1-4] in which all deserve highlight and of the many technological applications alkaline earth metal oxide (MgO) is also widely used in many technological applications such as: catalysis, toxic residue remediation, refractory ceramic glass additives, optically transparent, adsorbent for many pollutants, paints and superconductors, among others. MgO is a white hygroscopic solid mineral occurring naturally as periclase and as a non-toxic and environmentally correct material with high reactivity and adsorption capacities, and is a suitable adsorbent for aqueous solution cations and anions due to its favorable electrostatic attractive mechanism. In this work we investigated the properties of the adsorption processes of a urea molecule in an cluster of $(MgO)_{18}$ (Mg_9O_9)[5-9]. This model of MgO cluster allows us to investigate the urea adsorption energies at the three coordinating Mg (cluster cluster), four coordination (cluster cluster) and five (cluster cluster) coordination sites. The importance of urea (CH_4N_2O) as fertilizer[10] in the agricultural industry has grown enormously in recent years and according to all forecasts. We will analyze the molecular bonding energy CH_4N_2O-MgO, charge distribution, bond length, angles and dihedrons, highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), reactivity of molecular adsorption sites. Various methods of spectroscopy, IR spectroscopy, microwaves and Raman can provide information on the geometry of molecular structures. X-ray crystallography, neutron diffraction, and electron diffraction can provide information on the molecular structure for crystalline solids based on the distance between nuclei and the concentration of electron density. NMR methods can be used to determine information regarding the lengths of atomic bonds, angles and dehydrates.

Methods

In quantum chemistry, numerical analyzes are made with what is named "level theory" (LT) defined as the set of calculation procedures from the combination of methods and basis set. For all calculations we used Density Functional Theory (DFT) with WP04/6-31G(d,p) theory level[11-13] in Gaussian09 Package Program[14]. Figure 1 illustrates the systems studied, this is, (Figure 1-A) isolated urea molecule, (Figure 1-B) the urea molecule adsorbed on the corner of the MgO cluster, (Figure 1-C) the urea molecule adsorbed on the

edge of the MgO cluster and (Figure 1-D) the urea molecule adsorbed onto the surface of the MgO cluster with vacancy F. All optimization calculations were performed with the properties of the frozen MgO crystalline structure, ie, the distances of the adjacent atoms Mg-O of the cluster were kept constant at 2.106Å.
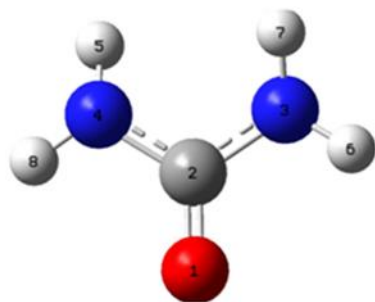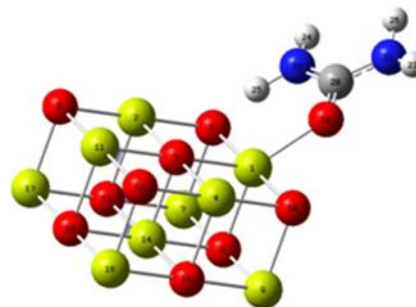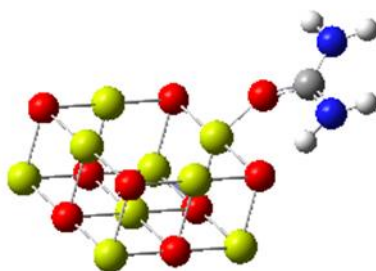

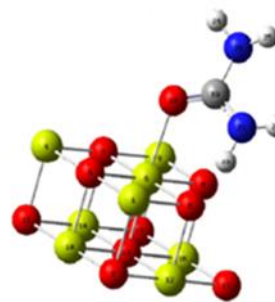Figure 1-A

Figure 1-B

Figure 1-C

Figure 1-D

The HOMO (Highest Occupied Molecular Orbital) shows the ability to donate an electron whereas LUMO (Lowest Unoccupied Molecular Orbital) as an electron acceptor shows the ability to obtain an electron. Both the HOMO and LUMO are the main orbitals that take part in chemical stability. The eigenvalues of LUMO and HOMO and their energy gap reflect the chemical activity of the molecule. Recently the energy gap between HOMO and LUMO orbital has been used to prove the bioactivity from intramolecular charge transfer[15,16].

An approximation for absolute hardness (ɳ)[17] (The hardness provides values on the resistance of the system to the transfer of electrons; the values given are generally positive; the hardness is closely linked to the band gap) was developed as ɳ=1/2(I-A) where (I) is the ionization energy (Ionization energy is the energy required to remove an electron from a system), (A) the electron affinity. According to the Koopman's theorem [18] we have $I=-E(HOMO)$ and $A=-E(LUMO)$ where E(HOMO) is the energy of the highest occupied molecular orbital and E(LUMO) is the energy of the lowest unoccupied molecular orbital. A higher (or less) HOMO energy corresponds to the more reactive molecule in reaction with electrophiles, while lower LUMO energy is essential for molecular reaction with nucleophiles. The global electron affinity (A) and ionization energy (I) are used to calculate another global reactivity descriptor, the electronic chemical potential (µ)[19] (The chemical potential promotes quantitative values related to the tendency of the electrons to escape from a system; usually the

values are negative) defined as $\mu=1/2(I+A)$, while the global philicity index (ω)[20] can be evaluated using the electronic chemical potential and chemical hardness (η)[33] as $\omega=\mu^2/2\eta$ (Electrophilicity promotes quantitative results on the electronic absorption capacity of a system). Table 01 summarize the results above cited for urea molecule isolated CH_4N_2O, isolated $MgO_{(core)}$, isolated $MgO_{(core-vac)}$ (cluster of MgO with vacancy F), (Mg_{3c})-urea (molecule of adsorbed urea on a coordinating Mg atom three of the cluster of MgO), (Mg_{4c})-urea (molecule of adsorbed urea on a coordinating Mg atom four of the cluster of MgO) and (Mg_{vac})-urea (molecule of adsorbed urea on a coordinating Mg atom surface vacant of the cluster of MgO).

Analysis of the distribution of electronic charges by the various atoms of a molecule is of fundamental importance to analyze the reactivity of atomic sites in a molecule (local reactivity). Although the concept of "atomic charge" in a molecule is not an observable quantum chemistry greatness, atomic charges has been a key concept for understanding a large number of chemical reactions, as well as being of fundamental importance for the understanding of a range of phenomena, such as dipole moments, chemical shifts in nuclear magnetic resonance (NMR), structures and molecular properties. Because of its great importance a large number of theoretical and experimental contributions have been proposed [34-36] for a better understanding of the atomic charges distributions in a molecules.

Analysis of Mulliken has the advantage of simplicity because its populations overlap divided equally between the two atoms of a bond and therefore. However it promotes a number of results that come at odds with expectations [37-40]. The electrostatic potential approach, has been far more promising, assigns point charges at atomic centers in order to best reproduce the electrostatic potential. Here, the main weakness is that the molecular electrostatic arises in a much more subtle and nonisotropic density than can be explained by a simple set of atom-centered point charges. Another promising method for the proposed load distribution in atoms in molecules has been "natural atomic charges" that has proven to be independent of the wave functions used in the calculations[38,41-42]. As expected Mulliken is more dependent on the basis set. Merhz-Kollman and NBO shows almost the same trend for the atomic charges. In table 3 are presents the atomic charges of the systems studied. In the table Mulliken means Mulliken charges, MK means Merhz-Kollman and NBO means Natural Bond Orders. Figure 2 illustrates in summary the values contained in table 3.

To describe the site reactivity or site selectivity, Yang et al.57 proposed the atom condensed Fukui function, based on the idea of electronic population around an atom in a molecule, similar to the procedure followed in the population analysis technique. The condensed Fukui function for an atom k undergoing nucleophilic (f_k^+), electrophilic (f_k^-), or radical attack (f_k^o). The Table 4 are present this values and Table 5 are present the relevant relations as support for analysis of values. The condensed-to-atom Fukui functions (f_k) at the atom k are usually evaluated from differences in atomic charges

$$f_k^+ = q_k(N+1) - q_k(N) \tag{1}$$
$$f_k^- = q_k(N) - q_k(N-1) \tag{2}$$
$$f_k^o = 1/2[q_k(N+1) - q_k(N-1)] \tag{3}$$

where q_k is the electronic charge of atom k and N is the number of electrons. From the interpretation given to the Fukui function relation $\Delta f_k = f_k^+ - f_k^-$ descriptor

[29,30] is very important to characterize the reactivity of a site within a molecule toward a nucleophilic or an electrophilic attack [29,30]. When $\Delta f_k > 0$ then the site is favored for a nucleophilic attack, whereas if $\Delta f_k < 0$ then the site may be favored for an electrophilic attack. Thus, with the numerical results of Δf_k we see, through Table 4, that the oxygen atom of the urea molecule has a much more appreciated electrophilic character while in the isolated urea molecule and it loses this character as the molecule of urea is adsorbed at the different sites of the MgO cluster. The carbon atom has an electrophilic character in the isolated molecule of urea, in a relation far less than the oxygen atom, but also loses electrophilic character as it adsorbs to MgO. The two nitrogen atoms are the ones that present the highest electrophilic in the solubility of urea molecule and completely lose that character, changing to the character nucleophilic attack in Mg_{4c}-Urea. Hydrogen atoms follow by a nucleophilic character suffering variations but with a high nucleophilic degree in Mg_{4c}-Urea.

Results

The binding energy BE of our MgO-urea study systems were calculated using the total energies of the, optimized systems, based on the expression:

$$BE = E_{tot}(MgO - Urea) - [E_{tot}(MgO) + E_{tot}(Urea)] \qquad (4)$$

so that

$$BE[MgO_{2c} - Urea] = BE[MgO_{4c} - Urea] = -9.0x10^{-8}eV$$
$$\text{and } BE[MgO_{vac} - Urea] = 0.0eV.$$

Table 1 shows how much the overall reactivity properties in the systems studied and therefore the urgency of careful studies for the understanding of the molecular adsorption processes in MgO clusters. The results of Table 1 are in electron-volt units. This table shows values demonstrating how much the values on the global indices are affected with the interaction of the urea molecule with the MgO cluster. In reference to the clusters of MgO it is seen that the vacancy greatly changes the index values. A higher (or less) HOMO energy corresponds to the more reactive molecule in reaction with electrophiles, while lower LUMO energy is essential for molecular reaction with nucleophiles. The Table 1 shows that energy required (I) to remove an electron from a urea molecule is bigger than the other systems. $MgO_{(core-vac)}$ raises ionization potential by approximately 8% that $MgO_{(core)}$ and the adsorption processes of the urea molecule with the MgO clusters further reduce the ionization potential of the systems and the adsorption processes of the urea molecule with the MgO clusters further reduces the ionization potential of the systems at the adsorption sites urea-(Mg_{3c}) and urea-(Mg_{4c}) while urea-(Mg_{vac}) presents values close to the $MgO_{(core-vac)}$ which brings us to the urea-(Mg_{vac}) binding energy closed at 0.0eV.

The electronic affinity (A), Table 1, presents much greater variations than the ionization energy (I) for the different studied systems, which shows that the different atomic positions significantly influence the E(LUMO) values. The chemical potential (μ), the absolute hardness (η) and global philicity index (ω), because they are proportional to E(HOMO) and E(LUMO), they are strongly influenced by the geometric structures of the systems studied.

Table 1 Values of Reactivity descriptors for isolated urea molecule and isolated regular $MgO_{(core)}$ and vacant $MgO_{(core-vac)}$ and for adsorption systems urea-(Mg_{3c}), urea-(Mg_{4c}), urea-(Mg_{vac})

Structure	I	A	η	μ	ω
Urea	7.641	-0.080	3.860	3.780	1.851
$MgO_{(core)}$	6.064	3.536	1.264	4.800	9.114
$MgO_{(core-vac)}$	6.595	6.196	0.100	6.396	204.544
Urea -(Mg_{3c})	5.616	3.530	1.043	4.573	10.025
Urea -(Mg_{4c})	5.522	3.431	1.046	4.476	9.558
Urea - (Mg_{vac})	6.533	6.115	0.419	6.324	47.724

Urea means isolated urea molecule. $MgO_{(core)}$ means regular MgO cluster. urea-(Mg_{3c}) means urea adsorbed on the coordination site three of MgO. Urea-(Mg_{4c}) means urea adsorbed on the coordination site four of MgO. Urea-(Mg_{vac}) means urea adsorbed on surface of MgO vacant.

The geometric properties, length of atomic bonds, angles and dihedra, of atomic molecules and clusters are very important and result from the values of the physical and chemical quantities of these systems. The presentation of these values can even be verified by several experimental techniques of spectroscopies. Table 2 shows the values for length of atomic bonds, angles of atomic bonds in degrees and degrees of atomic bonds in degrees, all of the urea molecule, for (Figure 1-A) urea molecule isolated CH_4N_2O, (Figure 1-B) (Mg_{3c})-Urea (molecule of adsorbed urea on a coordinating Mg atom three of the cluster of MgO), (Figure 1-C) (Mg_{4c})-Urea (molecule of adsorbed urea on a coordinating Mg atom four of the cluster of MgO) and (Figure 1-D) (Mgvac)-Urea (molecule of adsorbed urea on a coordinating Mg atom surface vacant of the cluster of MgO). The position of each atom is determined by the nature of the chemical bonds by which it is connected to its neighboring atoms. Molecular geometry can be described by the positions of these atoms in space, evoking bond lengths of two joined atoms, bond angles of three connected atoms and torsion angles (dihedral angles) of three consecutive bonds. We see in table 2 that the bond lengths of the atoms of the urea molecule undergo variations when adsorbed, as indicated by table 2, to the MgO atoms.

Table 2 Geometric Properties, Length (Å), Angle (o) and Dihedral (o) of atomic bonds of isolated and adsorbed urea molecule in Mg3c, Mg4c and (MgO)vac of the Mg9O9 adsorption sites.

	Length of Atomic Bonds		
Type	Urea	Urea-Mg$_{3c}$	Urea-Mg$_{4c}$	Urea-(MgO)$_{vac}$
O(1)-C(2)	1.1986	1.2383	1.2304	1.2236
C(2)-N(3)	1.3573	1.3136	1.3542	1.4700
C(2)-N(4)	1.3573	1.3327	1.3103	1.3195
N(4)-H(5)	0.9803	0.9775	0.9800	0.9800
N(3)-H(6)	0.9800	1.0458	0.9791	1.0341
N(3)-H(7)	0.9801	0.9791	1.0812	0.9797
N(4)-H(8)	0.9800	0.9785	0.9792	0.9800
	Angles of Atomic Bonds		
Type	Urea	Urea-Mg$_{3c}$	Urea-Mg$_{4c}$	Urea-(MgO)$_{vac}$
O(1)-C(2)-N(3)	122.8878	121.3337	118.2672	119.7222
C(2)-N(3)- N(4)	122.8977	118.7406	122.2529	122.6927
C(2)-N(4)-H(5)	118.9234	122.7938	115.2626	199.0037
C(2)-H(3)-H(6)	113.6288	117.3058	120.2713	114.5660
C(2)-H(3)-H(7)	118.9445	120.2866	113.5494	114.9891
C(2)-H(3)-H(8)	113.6287	117.9916	120.0461	119.2434
	Degrees of atomic bonds		
Type	Urea	Urea-Mg$_{3c}$	Urea-Mg$_{4c}$	Urea-(MgO)$_{vac}$
N(4)-C(2)-O(1)-N(3)	-179.9979	-179.3085	-178.4001	-179.5629
H(5)-N(4)-C(2)-O(1)	-152.3806	-176.3990	-160.9966	158.2554
H(6)-N(3)-C(2)-O(1)	-11.9952	0.6579	-0.6340	10.5042
H(7)-N(3)-C(2)-O(1)	-152.4229	176.1776	-177.9780	160.9263
H(8)-N(4)-C(2)-O(1)	-12.0521	-4.7637	-13.5368	14.3100

Urea means isolated urea molecule. Urea-(Mg$_{3c}$) means urea adsorbed on the coordination site three of MgO. Urea-Mg$_{4c}$ means urea adsorbed on the coordination site four of MgO. Urea-(MgO)$_{vac}$ means urea adsorbed on surface on the coordination site five of MgO vacant.

We kept the same DFT//WP04/6-31G(d,p) theory level in all our calculations and we see in Table 3 that the values of atomic charges vary with the variation of the systems studied. This demonstrates the great relevance of using more than one method of calculations to obtain the results on the variation of atomic charges. The variations in atomic charges studied in our systems of the urea molecule adsorption processes are obviously a phenomenon of induction by physical processes pertinent to changes in the urea molecule adsorption sites in the MgO cluster with or without vacancy. We use the illustration of atomic charge values presented in Table 3 for a better qualitative understanding of charge distributions. In both figures and Table 3, we see that the atomic charges calculated using the Mulliken method show significant variations directly dependent on the studied system. All three methods used show that the MgO cluster promotes a variation of atomic charges always to more positive when the original charges are positive and to more negative when the original charges are negative with the exception of the vacant MgO system. The success of a description of the quantum mechanics of a molecule is generally assessed by its ability to correctly reproduce an observable amount, such as spectroscopic information, rotational barriers, conformations, etc. However, different approaches to quantum mechanics, although each may succeed in their own are known to generate charge distributions that vary depending on the method. The results on our load variations show that the three methods used are influenced by

the model of the systems studied. Table 3 shows that in all three methods, Mulliken, Merz-Kolman and Natural Bond Order, there was no significant variation in the total charge of the Urea molecule in the MgO adsorption sites, but small variations in the second decimal place of the total charge values of the molecule of Urea.

Table 3 Atomic charges of Mulliken, Merz-Kolman (MK) and Natural Bond Order (NBO) of the urea molecule isolated and adsorbed on the respective Mg_9O_9 adsorption sites.

|	Urea Molecule			Urea at the corner of MgO		
	Mulliken	MK	NBO	Mulliken	MK	NBO
O	-0.5113	-0.6248	-0.6893	-0.7026	-0.7125	-0.8041
C	0.7469	0.9436	0.8462	0.9048	0.9242	0.8328
N	0.2106	-0.9478	-0.8760	-0.6988	-0.9978	-0.8636
N	0.2100	-0.9468	-0.8761	-0.6569	-0.8744	-0.8446
H	-0.1974	0.3933	0.3891	0.2745	0.3941	0.4094
H	-0.1308	0.3963	0.4086	0.4179	0.5344	0.4481
H	-0.1975	0.3920	0.3891	0.2514	0.4015	0.3956
H	-0.1305	0.3140	0.4085	0.3020	0.3997	0.4298
	Urea on the edge of MgO			Urea on the vacant MgO		
	Mulliken	MK	NBO	Mulliken	MK	NBO
O	-0.6463	-0.6458	-0.7604	-0.5990	-0.8551	-0.7223
C	0.8278	0.9165	0.8222	0.8070	1.1485	0.8473
N	-0.6545	-0.9123	-0.8711	-0.6831	-1.0920	-0.9166
N	-0.6941	-1.0577	-0.8782	-0.6571	-1.3403	-0.8523
H	0.2865	0.3802	0.4166	0.2539	0.5010	0.3965
H	0.2286	0.3979	0.3828	0.4376	0.8141	0.4679
H	0.4401	0.6295	0.4751	0.2687	0.4233	0.4032
H	0.2539	0.3766	0.3931	0.2567	0.4215	0.3939
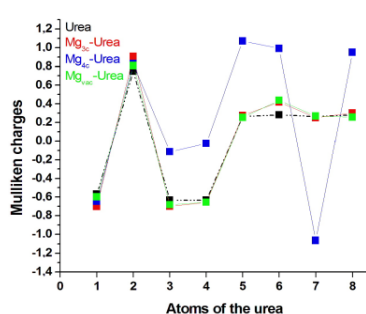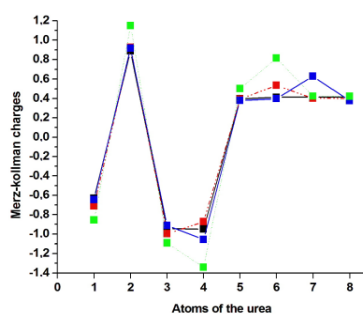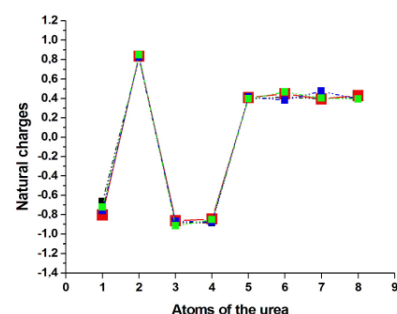
Figure 2-A   Figure 2-B   Figure 2-C

Fukui indices are types of molecular descriptors capable of providing us with information about which atoms in a molecule are more likely to lose or accept an electron, which we interpret as more likely to suffer a nucleophilic or electrophilic attack, respectively. This, in turn, has to do with a tendency of the molecule to polarize in the presence of an external field or by changing the density of electrons. Table 4 shows that the atoms of the isolated Urea molecule show significant values of the Fukui ices and that they are lost when adsorbed on the MgO cluster. We see that only the nitrogen and hydrogen atoms of the Urea molecule have significant values for the Fukui indices in the Mg4c-urea system.

As we are dealing with occupation numbers in each atom, these indexes are very sensitive to changes in the sets of bases and in the population analysis paradigm. It is important that you never take these numbers as absolute, just as comparative parameters within the same system. It is also very appropriate for calculations to be made using more than one method and one level of theory to further confirm or even ignore the observed trends, for example, natural population analysis is much more robust than the Mulliken method.

Table 4 Values of the Fukui function considering the Mulliken charges calculated with equations (1-3),

		Urea Molecule			Mg$_{3c}$-urea			Mg$_{4c}$-urea			Mg$_{vac}$-urea		
		f_k^+	f_k^-	f_k^0	f_k^+	f_k^-	f_k^0	f_k^+	f_k^-	f_k^0	f_k^+	f_k^-	f_k^0
1	O	0.063	0.364	0.214	0.006	-0.002	0.002	-0.005	-0.021	-0.013	0.009	0.000	0.004
2	C	0.079	0.086	0.083	0.010	0.005	0.008	0.004	0.007	0.006	0.006	0.012	0.009
3	N	-0.207	0.119	-0.044	-0.019	-0.007	-0.013	0.547	-0.530	0.009	0.008	0.012	0.010
4	N	-0.215	0.119	-0.048	0.008	0.011	0.010	0.661	-0.667	-0.003	0.001	0.004	0.003
5	H	0.381	0.084	0.233	0.009	0.013	0.011	0.793	-0.779	0.007	0.023	0.021	0.022
6	H	0.267	0.072	0.170	-0.019	-0.004	-0.012	0.780	-0.744	0.017	-0.002	-0.011	-0.006
7	H	0.359	0.084	0.222	0.005	0.015	0.010	0.624	-0.623	0.001	0.015	0.017	0.016
8	H	0.275	0.072	0.174	0.014	0.011	0.012	0.707	-0.679	0.014	0.021	0.019	0.020

Orbital analysis of natural bonding provides an efficient method for studying intra and inter-molecular bonds and interactions between bonds and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. Some orbitals from donors electrons, acceptor orbitals and interacting stabilization energy resulting from the second order micro-disturbance theory [66], For each donor (*i*) and acceptor (*j*), the stabilization energy E(2) associated with relocation *i, j* estimated as:

$$E_2 = \Delta E_{ij} = q_i \frac{F(i,j)^2}{E_i - E_j}$$

where q_i is the donor orbital occupancy, E_i and E_j are diagonal elements and F(i,j) is the off-diagonal NBO Fock matrix elements. The higher the value of E(2), the more intense is the interaction between electron donors and electron acceptors.

In Table 5 (values for the isolated urea molecule), the expressive values of E(2), presented in the third column of the table, are those referring to $n_{(2)-O_1} \rightarrow \sigma^*_{c2-N3}$ and $n_{(2)-O_1} \rightarrow \sigma^*_{c2-N4}$ in which, for both, E(2)=25,14*kcal/mol*, deserve our special attention by comparison with the other values. The stabilization values originate from the reason that the energy gap $\Delta E_{ij} = E_i - E_j$ is small (0.66au) and due to the fact that the interaction elements F_{ij} are large (0.117au).

Table 5 NBO Analysis of Hyperconjugative Interaction in Isolated Urea Molecule

Donor Orbital(i)		Acceptor Orbital(j)	(a)$E(2)$ Kcal/mol	(b)$E(j) - E(i)$ (au)	(c)F_{ij} (au)
σ_{O1-C2}	$\rightarrow$	σ^*_{C2-N3}	0.89	1.48	0.033
σ_{O1-C2}	$\rightarrow$	σ^*_{C2-N4}	0.89	1.48	0.033
σ_{O1-C2}	$\rightarrow$	σ^*_{N4-H7}	1.28	1.53	0.040
σ_{O1-C2}	$\rightarrow$	σ^*_{N4-H5}	1.27	1.53	0.039
π_{O1-C2}	$\rightarrow$	π^*_{O1-C2}	2.28	0.36	0.028
π_{O1-C2}	$\rightarrow$	σ^*_{N3-H7}	0.55	0.83	0.019
π_{O1-C2}	$\rightarrow$	σ^*_{N4-H5}	0.56	0.83	0.019
σ_{C2-N3}	$\rightarrow$	σ^*_{O1-C2}	0.64	1.43	0.027
σ_{C2-N4}	$\rightarrow$	σ^*_{O1-C2}	0.64	1.43	0.027
σ_{C2-N4}	$\rightarrow$	σ^*_{N3-H6}	2.12	1.32	0.047
σ_{N3-H6}	$\rightarrow$	σ^*_{C2-N4}	4.75	1.09	0.065
σ_{N3-H6}	$\rightarrow$	σ^*_{O1-C2}	4.31	1.29	0.067
σ_{N3-H7}	$\rightarrow$	σ^*_{O1-C2}	0.75	0.68	0.022
σ_{N4-H5}	$\rightarrow$	σ^*_{O1-C2}	4.30	1.29	0.067
σ_{N4-H5}	$\rightarrow$	π^*_{O1-C2}	0.77	0.68	0.022
σ_{N4-H8}	$\rightarrow$	σ^*_{C2-N3}	4.75	1.09	0.065
$n_{(1)-O1}$	$\rightarrow$	σ^*_{C2-N3}	2.17	1.09	0.044
$n_{(1)-O1}$	$\rightarrow$	σ^*_{C2-N4}	2.17	1.09	0.044
$n_{(2)-O1}$	$\rightarrow$	σ^*_{C2-N3}	25.14	0.66	0.117
$n_{(2)-O1}$	$\rightarrow$	σ^*_{C2-N4}	25.14	0.66	0.117

(a)E(2) is the energy of hyper conjugative interaction, stabilization energies;

(b)Is the energy difference between donor and acceptor i and j NBO orbitals;

(c)F(i,j) is the Fock matrix element between i and j NBO orbitals,

In Table 6 (values for the urea molecule adsorbed on the respective MgO adsorption sites). In Mg3c-Urea system we get that $n_{(2)-O_{19}} \rightarrow \sigma^*_{c20-N22}$ [E(2)=100.39kcal/mol, Δ E$_{ij}$=0.23au, F$_{ij}$=0,144au] and $n_{(1)-N_{21}} \rightarrow \sigma^*_{c20-N22}$ [E(2)=95.47kcal/mol), Δ E$_{ij}$=0.20au, F$_{ij}$=0.133au], are the two of expressive values Donor$\rightarrow$ Acceptor orbitals for stabilization energy E(2). There is, in Mg$_{3c}$-Urea, the presence of n$_{(1)}$ differently from the isolated urea molecule. The trend of Mg$_{3c\text{-Urea}}$ continues towards Mg$_{4c\text{-Urea}}$ but in Mg$_{vac\text{-Urea}}$ there is the presence of $n_{(3)-O_{18}} \rightarrow \sigma^*_{c19-N20}$ [E(2)=111.40kcal/mol, Δ E$_{ij}$=0.21au, F$_{ij}$=0.145au].

Table 6 NBO Analysis of Hyperconjugative Interaction in Mg_{3c}-urea, Mg_{4c}-urea and Mg_{vac}-urea.

Donor Orbital (i)	Acceptor Orbital (j)	(a)$E(2)$ Kcal/mol	(b)$E(j) - E(i)$ (au)	(c)F_{ij} (au)
$\sigma_{Mg1-O19} \rightarrow$	$\sigma^*_{C20-N21}$	5.26	0.93	0.063
$\sigma_{Mg1-O19}$	$\pi^*_{C20-N22}$	15.40	0.91	0.106
$n_{(2)-O19}$	$\sigma^*_{C20-N22}$	100.39	0.23	0.144
$n_{(1)-N21}$	$\sigma^*_{C20-N22}$	95.47	0.20	0.133
$\sigma_{Mg1-O19}$	$\sigma^*_{C20-N21}$	6.37	0.88	0.067
$\sigma_{Mg1-O19}$	$\pi^*_{C20-N22}$	17.48	0.82	0.107
$n_{(2)-O19}$	$\sigma^*_{C20-N21}$	107.98	0.23	0.150
$n_{(1)-N22}$	$\sigma^*_{C20-N21}$	107.91	0.20	0.142
σ_{Mg6-O5}	$\sigma^*_{N21-H23}$	20.03	1.20	0.139
$n_{(1)-O18}$	$n^*_{(1)-Mg6}$	17.93	0.84	0.112
$n_{(3)-O18}$	$\sigma^*_{C19-N20}$	111.40	0.21	0.145
$n_{(1)-N21}$	$\sigma^*_{C19-N20}$	79.54	0.19	0.121

Figures 3, 4 and 5 present the spectra, IR spectrum, VCD spectrum and Raman spectrum, for the investigated structures, Figure 3 shows the spectra for the MgO clusters without the adsorption of the urea molecule, Figure 4 shows the spectra for the isolated urea molecule, ie without adsorption with the MgO clusters, and Figure 5 shows the spectra for the adsorption processes of the urea molecule at the respective adsorption sites of the MgO clusters, Figure 3 shows that the frequency range (in cm^{-1}) of the MgO clusters is comprised of the intervals $[150 - 522.64]cm^{-1}$ for the regular MgO cluster and $[20.82 - 486.35]cm^{-1}$ to the vacant MgO cluster, Figure 4 shows the spectra for the urea molecule whose values of the vibrations of the atomic groups are shown in Table 7, Figure 5 shows the spectra for the adsorption modes of the urea molecule in the MgO cluster whose values of the vibrations of the atomic groups are shown in Table 7, The figures and Table 7 show significant changes in the spectra and in the vibrational states of the groups of atoms of the urea molecule as it is adsorbed at the different atomic sites of the pure or vacant MgO cluster.
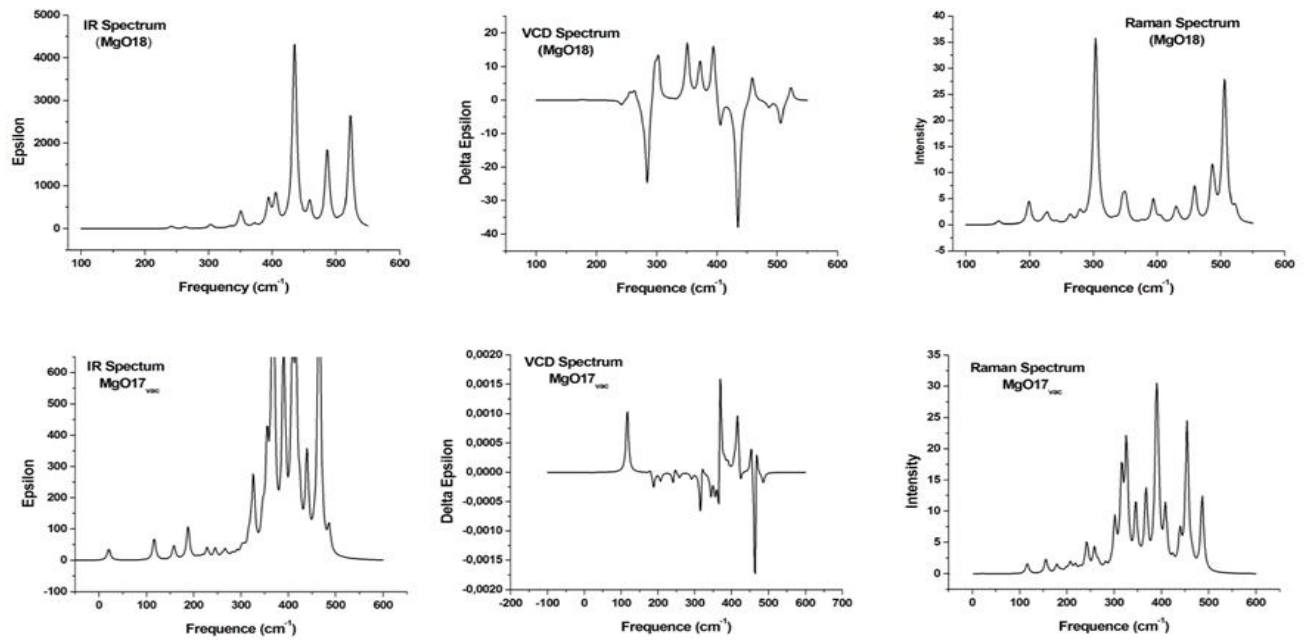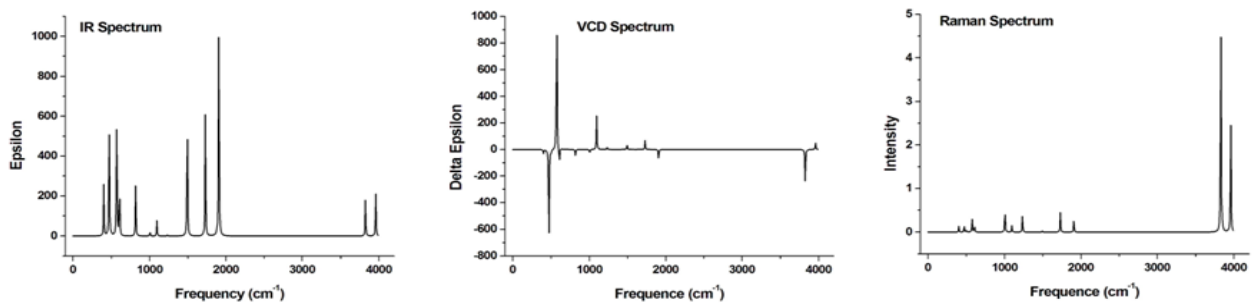
Figure 3 – Core MgO Spectrum
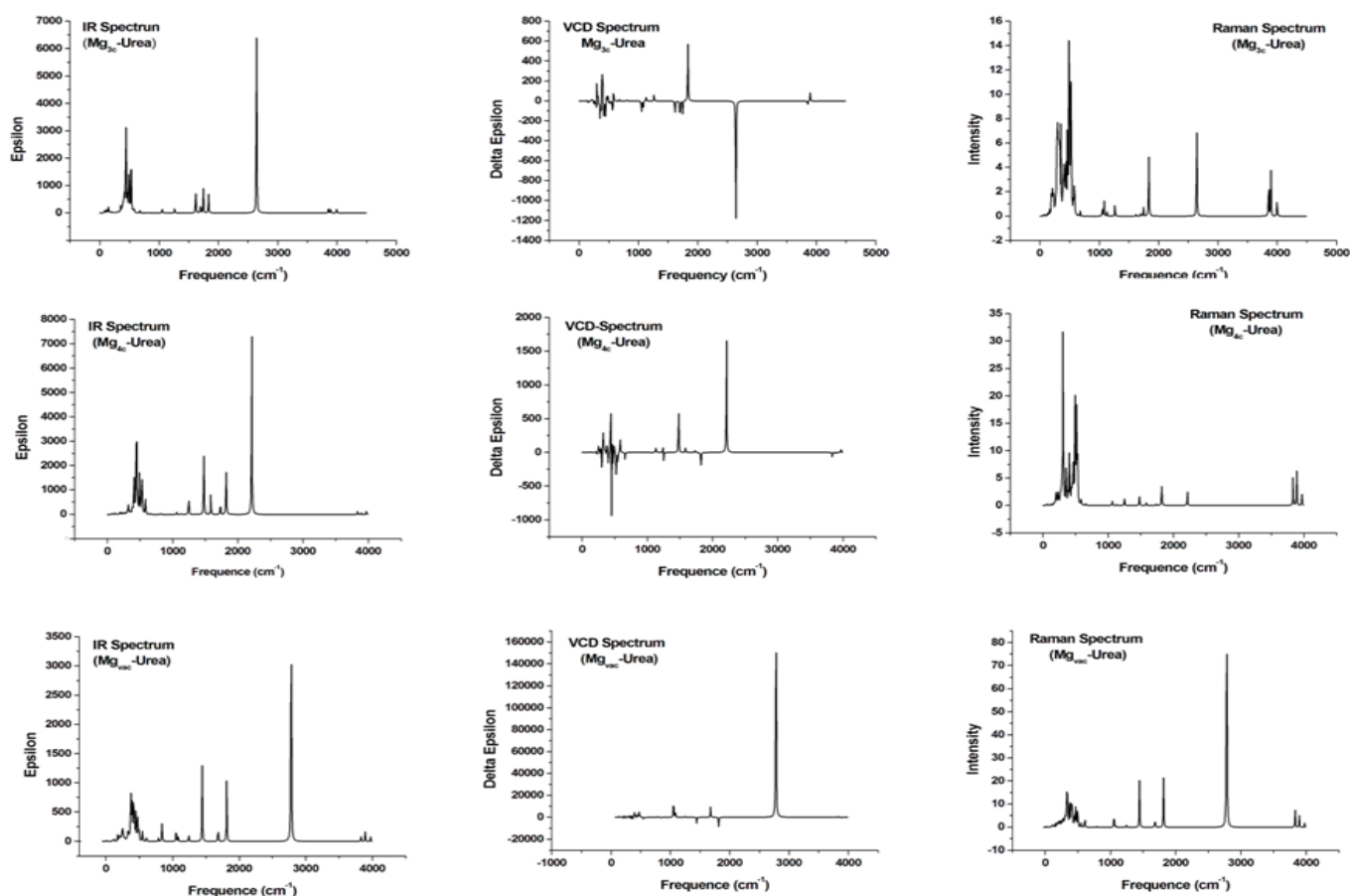

Figure 4-Urea Molecule Spectrum

Figure 5 MgO-Urea Spectrum

Table 7   Vibrational Frequencies (cm^{-1})

Atomics Groups	Urea	Mg$_{3c}$-Urea	Mg$_{4c}$-Urea	Mg$_{vac}$-Urea
$N = C$	1004.89	1617.26	1061.90	842.40
$C = O$	1728.35	1696.50	1820.82	1812.16
$N = C = O$	1906.48	1833.03	1585.19	1443.80
$N - H$	3824.46	3857.02	3832.04	2523.15

In the adsorption systems MgO-urea we see that the cluster vibrates, without the urea molecule vibrating, in the frequency ranges: (1) Mg$_{3c}$-urea [222.22-531.37]cm^{-1}(2) Mg$_{4c}$-urea [165.2—512.01]cm^{-1}e (3) Mg$_{vac}$-urea [16.47 -443.70]cm^{-1}. We see that even under very little connection energy the specta undergoes expressive changes in the vibrational modes of the systems.

Conclusions

The importance of urea as a soil fertilizer is indisputable as is the presence of various minerals in the composition of soil chemistry and physics, An understanding of the physical and chemical processes of urea adsorption with such minerals is of vital importance in various agricultural activities, In our work we chose to study the interaction of urea with MgO because it is an oxide that has been used in several fields of scientific activity and particularly in catalytic processes, This work, with its results, demonstrates the degree of complexity

contained in the studied systems, since despite the small binding energy of the urea molecule with the cluster of MgO its geometric properties, reactivities etc, are changed considerably, The density functional theory has given us a chance to investigate global and local reactivity properties through Fukui functions, electron transfer transfers, and bonding energies that allow deeper and more accurate analysis of complex interacting systems. The studies and results obtained here show that the interaction of the urea molecule with the MgO cluster promotes charge variations and reactivities directly related to the new electronic configurations of the atoms of the urea molecule without electronic exchanges of the urea molecule with the Mg_9O_9 cluster.

Acknowledgments:

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