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Interaction of NTO with Mg or/and Ca – DFT treatment

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Abstract

Interaction of NTO with Mg or/and Ca atom(s) has been investigated within the constraints of density functional theory at the level of B3LYP/ 6-311++G(d,p). The results revealed that the composites considered are exothermic and favorable in terms of Hº and Gº values. Also they are electronically stable. Various structural, quantum chemical and spectral (UV-VIS) data are collected and discussed. The metal atoms, in each case, acquired positive charge(s) but no bond density exists between the components of the composites. The UV-VIS spectra shifts to higher wavelengths as the calcium content increases in the composites.

1. Introduction

The most extensively studied nitrotriazole explosives, NTO, (5-Nitro-2,4-dihydro-3H-1,2,4-triazol-3-one) [1] possesses good thermal stability [2], low chemical sensitivity to radiation damage [3] and is relatively insensitive to impact and shock [4].

Various articles concerning NTO and its tautomers have been published [5-15]. It has been observed that NTO is less sensitive than RDX [13] and has captured a major role in research of energetic materials as one of the important insensitive high explosive having thermal stability, insensitivity to impact, friction, heat, spark and shock waves [14]. A key characteristic of NTO is its relatively easy synthesis. In addition to that it displays some performance characteristics comparable to those of the currently commonly employed secondary explosives and possesses some potential to be used as an explosive and propellant ingredient. It is to be mentioned that NTO has been shown to be less harmful to human health than the traditional explosives [15]. Additionally, it can be pressed without a binder into desired morphology having a high density [16]. Its particle size and morphology have tailored by several researchers in order to meet the requirements of formulations [17,18]. However, this nitrogen heterocyclic energetic compound presents some drawbacks, which limit its further applications (such as negative oxygen balance, negative enthalpy of formation and acidity). To overcome such kind of shortcomings, the researchers have adopted various approaches. One of them concerns the preparation of NTO derivatives owing to its acidity and the other one is the formation of NTO-co-crystals. The first approach is the famous one, where several metal and amine salts, and other derivatives of NTO have been produced and others continue to appear [19]. Certain metals including Al, Mg etc., are often involved in formulation of certain ammunition to increase the heat output of the composite [20]. The interaction of TATB and magnesium have been investigated quantum chemically within the limitations of density functional theory (DFT) at B3LYP/6-311++G(d,p) level [21]. Titanium is used in fountain fireworks as admixture of various energetic materials [22].

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In the present treatise, both the individual effects of magnesium or calcium atom and also their mutual effect on NTO molecule are considered within the restrictions of DFT and the basis set employed in vacuum conditions.

2. Method of Calculations

In the present study, all the initial optimizations of the structures leading to energy minima have been achieved first by using MM2 method which is then followed by semi empirical PM3 self consistent fields molecular orbital method [23-25]. Afterwards, the structure optimizations have been achieved within the framework of Hartree-Fock and finally by using density functional theory (DFT) at the level of B3LYP/6-311++G(d,p) [26,27]. Note that the exchange term of B3LYP consists of hybrid Hartree-Fock and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [28]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [29] and Lee, Yang, Parr (LYP) correlation correction functional [30]. In the present study, the normal mode analysis for each structure yielded no imaginary frequencies for the $3N–6$ vibrational degrees of freedom, where N is the number of atoms in the system. This search has indicated that the structure of each molecule considered corresponds to at least a local minimum on the potential energy surface. Furthermore, all the bond lengths have been thoroughly searched in order to find out whether any bond cleavages occurred or not during the geometry optimization process. All these computations were performed by using SPARTAN 06 program [31].

3. Results and Discussion

Quite often certain metals like aluminum, magnesium, zinc etc., are found in formulation of energetic materials in order to improve some properties of them, such as heat outputs [20].

Magnesium atom in its ground state has the electronic configuration of $1s^2 2s^2 2p^6 3s^2$ whereas calcium possesses $[Mg]3p^6 4s^2$.

Optimized structures of the composites considered are shown in Figure 1 which also displays the direction of the dipole moment vectors. The direction varies from one composite to other. The organic component in each composite undergoes some minute structural changes as the kind of metal components varies. Note that NTO+2Mg composite could not be constructed at the beginning thus it is not considered presently.

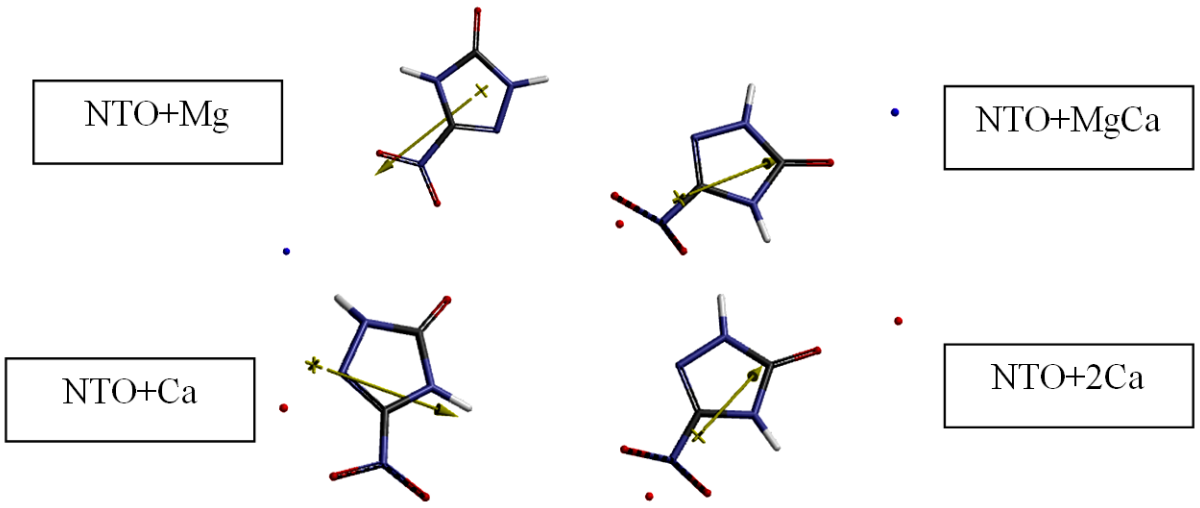

Figure 1. Optimized structures of the composites considered.

Table 1 list some thermo chemical properties of the composites considered. The data presented in the table reveal that the standard thermo chemical formation data of all the species considered are exothermic (H^o values) and they are favored according to their G^o (Gibbs free energy of formation) values.

Table 1. Some thermo chemical properties of the composites considered.

Composites	H^o	S^o (J/mol^o)	G^o
NTO+Mg	-1896037.662	377.80	-1896150.302
NTO+MgCa	-3675292.196	402.30	-3675412.156
NTO+Ca	-3149874.145	378.08	-3149986.858
NTO+2Ca	-4928995.402	405.32	-4929116.255

Energies in kJ/mol.

Table 2 shows some energies of the composites considered where E, ZPE and E_C stand for the total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively. According to the data, all the composites are electronically stable.

Table 2. Some energies of the composites considered.

Composites	E	ZPE	E_C
NTO+Mg	-1896217.65	174.30	-1896043.35
NTO+MgCa	-3675457.09	172.27	-3675284.82
NTO+Ca	-3150038.70	169.68	-3149869.02
NTO+2Ca	-4929150.48	174.16	-4928976.32

Energies in kJ/mol.

Table 3 includes some calculated properties of the composites considered. It is worth mentioning that the polar surface area (PSA) is defined as the amount of molecular surface area arising from polar atoms (N,O) together with their attached hydrogen atoms. The orders of dipole moment and polarizability values are the same except NTO+2Ca case.

Table 3. Some calculated properties of the composites considered.

Composites	Dipole	Molecular Wt.(amu)	Area (Å^2)	Volume (Å^3)	PSA (Å^2)	Ovality	Polarizability
NTO+Mg	2.25	154.37	147.09	105.92	92.03	1.36	49.67
NTO+MgCa	18.09	194.45	157.26	118.21	85.50	1.35	50.92
NTO+Ca	11.21	170.14	139.69	108.34	87.54	1.27	49.95
NTO+2Ca	8.36	210.22	160.61	121.89	83.28	1.35	51.19

Dipole moments in debye units. Polarizabilities in 10^{-30} m^3 units.

Figure 2 shows the electrostatic charges (ESP) on atoms of the composites considered. The ESP charges are obtained by the program based on a numerical method that generates charges that reproduce the electrostatic

potential field from the entire wavefunction [31]. Note that in each case the metal component(s) have some positive charge(s). In NTO+MgCa composite the magnesium atom acquires less charge than the calcium atom. The magnitudes of the charges are complicated function of many factors involving the fine topology. The first ionization energies of Mg and Ca are 736 kJ/mol. and 590 kJ/mol, respectively [32].

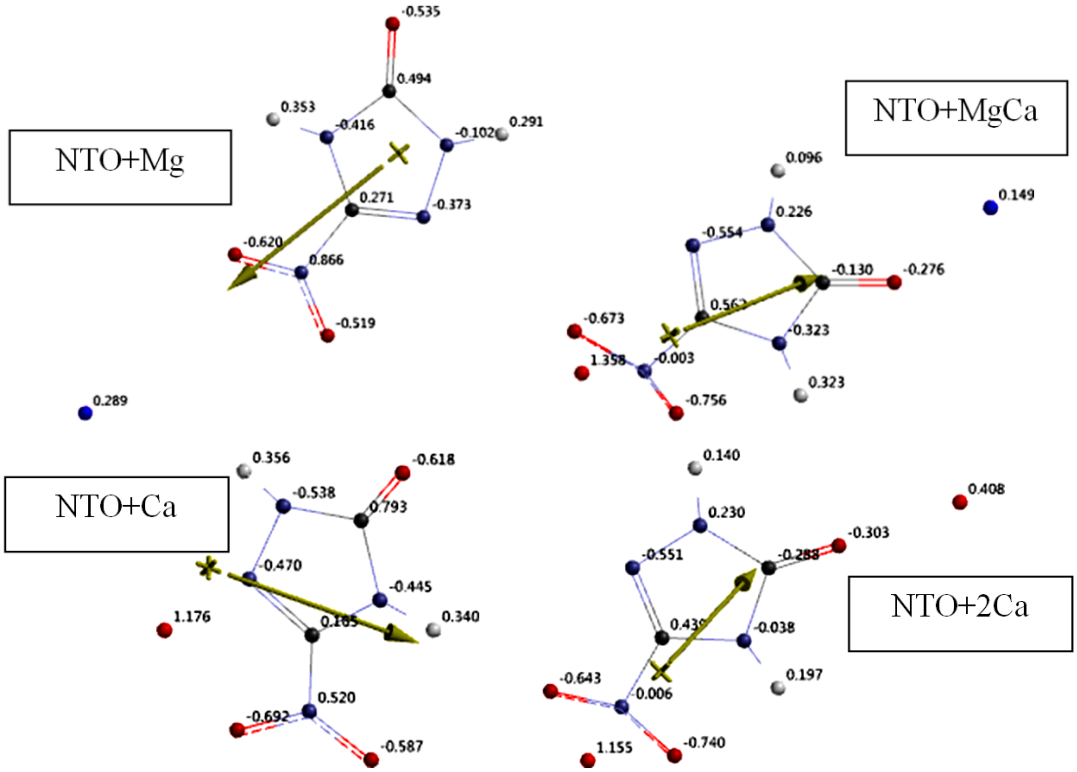

Figure 2. ESP charges on atoms of the composites considered.

Electrostatic potential maps of the composites considered are shown in Figure 3, where negative potential regions reside on red/reddish and positive ones on blue/bluish parts of the maps.

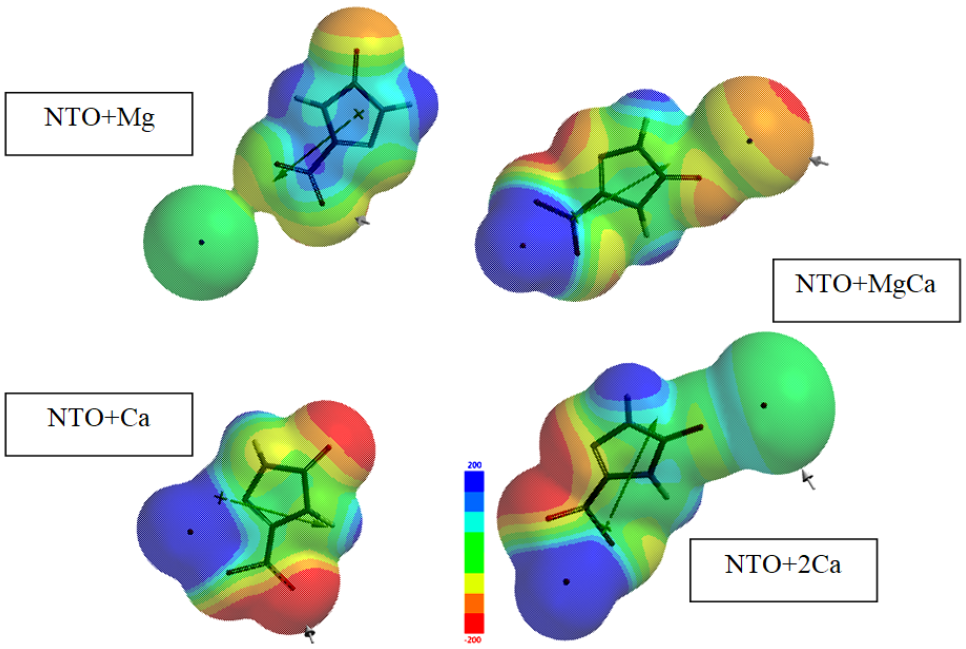

Figure 3. Electrostatic potential maps of the composites considered.

Note that the main blue (positive) region in the composites resides on the calcium atom whereas relatively more negative site coincides with the magnesium atom. In some of the composites N-H hydrogen atom (like NTO+Mg composite) falls in to the blue region depending on the electron distribution within the organic component arising from the effect of the metal atom(s).

Figure 4 is the bond densities of the composites considered. As seen in the figure, in all the cases there is no bond density in between the inorganic and organic components of the composites.

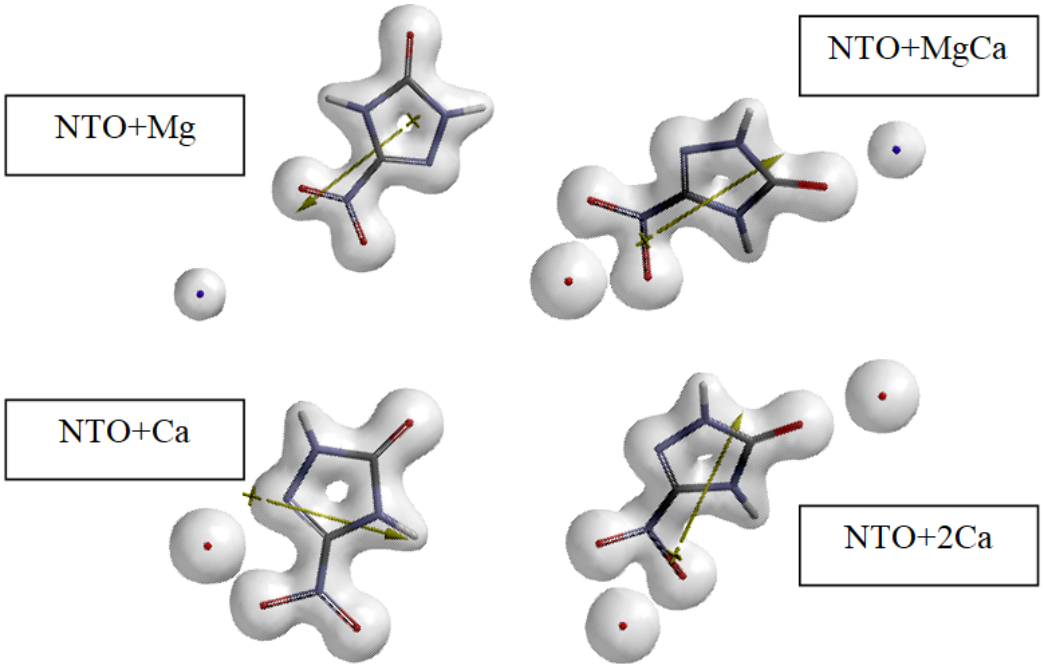

Figure 4. Bond densities of the composites considered.

Figure 5 shows the local ionization maps of the composites considered where conventionally red/reddish

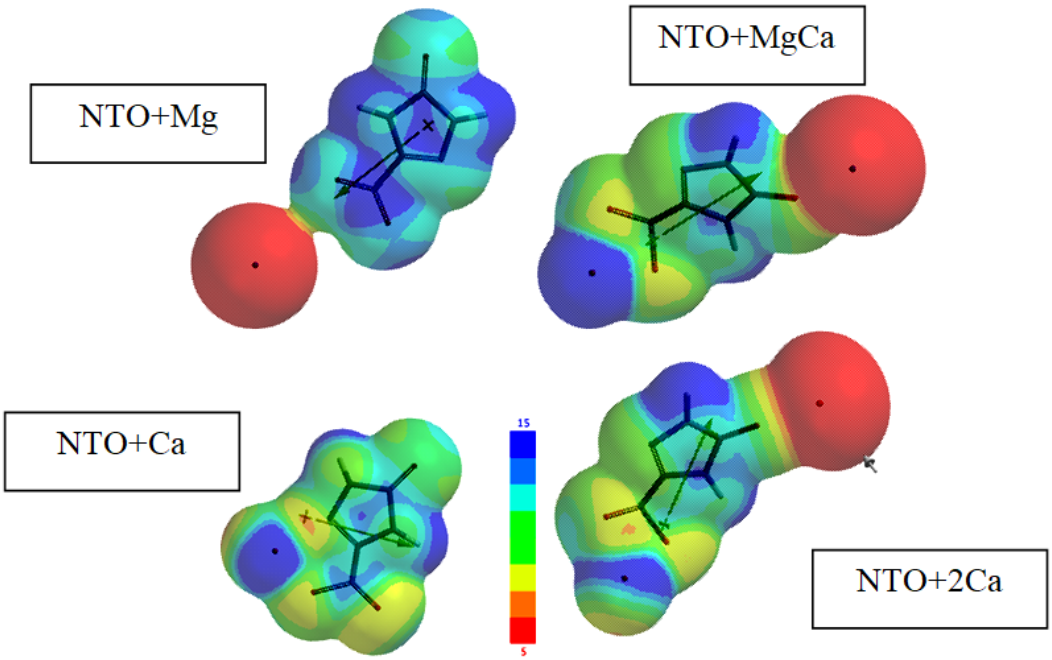

Figure 5. Local ionization maps of the composites considered.

regions (if any exists) on the density surface indicate areas from which electron removal is relatively easy, meaning that they are subject to electrophilic attack. It is worth remembering that the local ionization potential map is a graph of the value of the local ionization potential on an isodensity surface corresponding to a van der Waals surface.

The LUMO maps of the composites considered are shown in Figure 6. Note that a LUMO map displays the absolute value of the LUMO on the electron density surface. The blue color (if any exists) stands for the maximum value of the LUMO and the red colored region, associates with the minimum value. Note that the LUMO and NEXTLUMO are the major orbitals directing the molecule towards the attack of nucleophiles [31]. Positions where the greatest LUMO coefficient exists is the most vulnerable site in nucleophilic reactions.

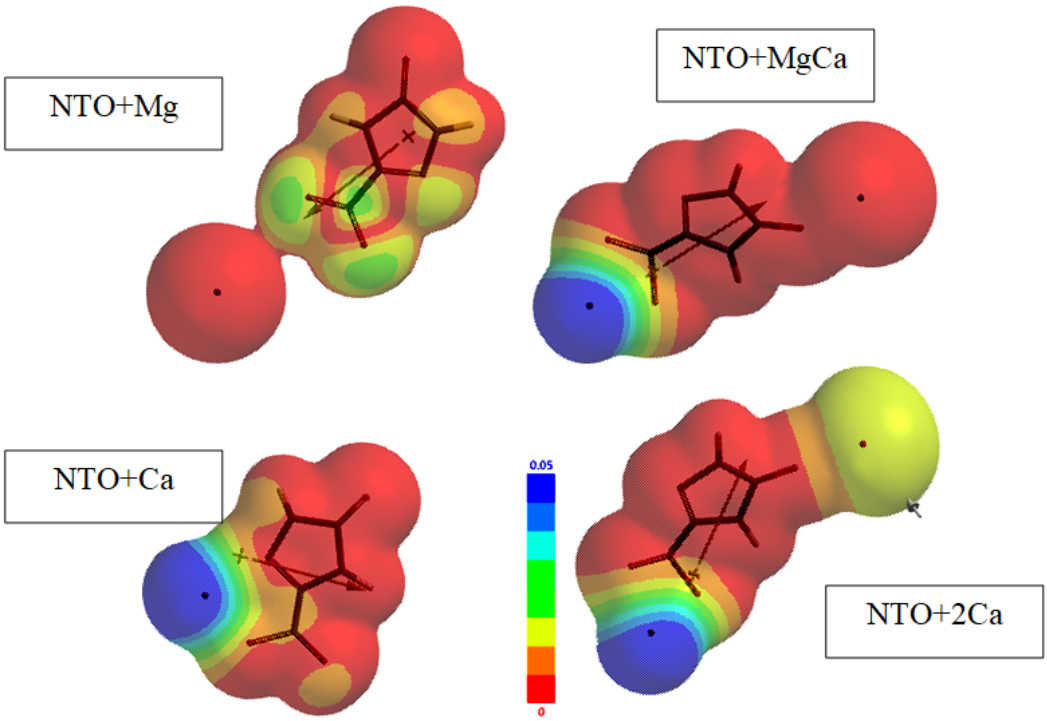

Figure 6. The LUMO maps of the composites considered.

Some of the molecular orbital energy levels of the composites considered are displayed in Figure 7. Note that that the inner lying molecular orbitals are assumed to be responsible for the thermal stability. Also, it is to be noticed that the closely lying HOMO and LUMO energy levels occur in the cases of NTO+MgCa and NTO+2Ca composites.

Table 4 lists the HOMO and LUMO energies and the interfrontier molecular orbital energy gap, $\Delta\varepsilon$ ($\Delta\varepsilon = \varepsilon_{LUMO}-\varepsilon_{HOMO}$) values of the composites considered. The algebraic orders of the HOMO and LUMO energies are the same as, NTO+Mg< NTO+Ca< NTO+MgCa< NTO+2Ca. Whereas, the interfrontier molecular orbital energy gap values, constitute the order of NTO+Mg > NTO+Ca> NTO+2Ca > NTO+MgCa.

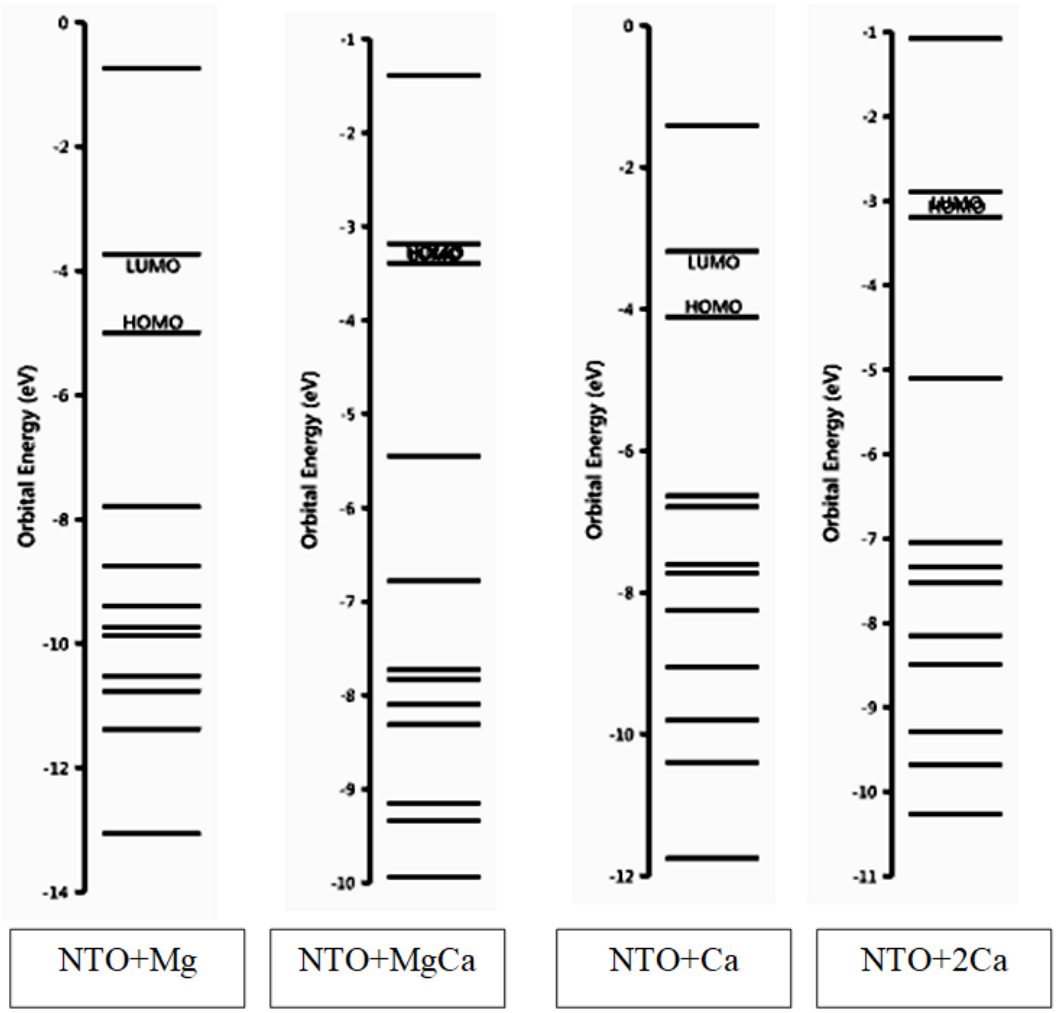

Figure 7. Some of the molecular orbital energy levels of the composites considered.

Table 4. The HOMO and LUMO energies and Δε values of the composites considered.

Composites	HOMO	LUMO	Δε
NTO+Mg	-482.35	-360.44	121.91
NTO+MgCa	-326.95	-306.85	20.10
NTO+Ca	-396.79	-307.05	89.74
NTO+2Ca	-308.22	-279.01	29.21

Energies in kJ/mol.

As the order of Δε values indicates, the mixed composite, NTO+MgCa, has the smallest interfrontier molecular energy gap. Thus, any ballistic property which correlates with the narrowness of it should have the highest value among the composites considered. An example is the impact sensitivity, that is narrower the gap, the explosive becomes more sensitive to an impact stimulus [33,34].

Figure 8 displays the HOMO and LUMO patterns, whereas the NextHOMO (NHOMO, HOMO-1) and NextLUMO (NLUMO, LUMO+1) patters of the composite systems considered are shown in Figure 9.

In the case of NTO+Mg, the magnesium atom makes a great contribution to the HOMO whereas nothing to the LUMO. Also the contribution of NTO is nil to the LUMO. In NTO+MgCa case the magnesium is the main contributor to the HOMO whereas the calcium does not take any part. The roles of the metals are conversed in the LUMO, that is the calcium greatly contributes whereas the magnesium does not participate into the LUMO.

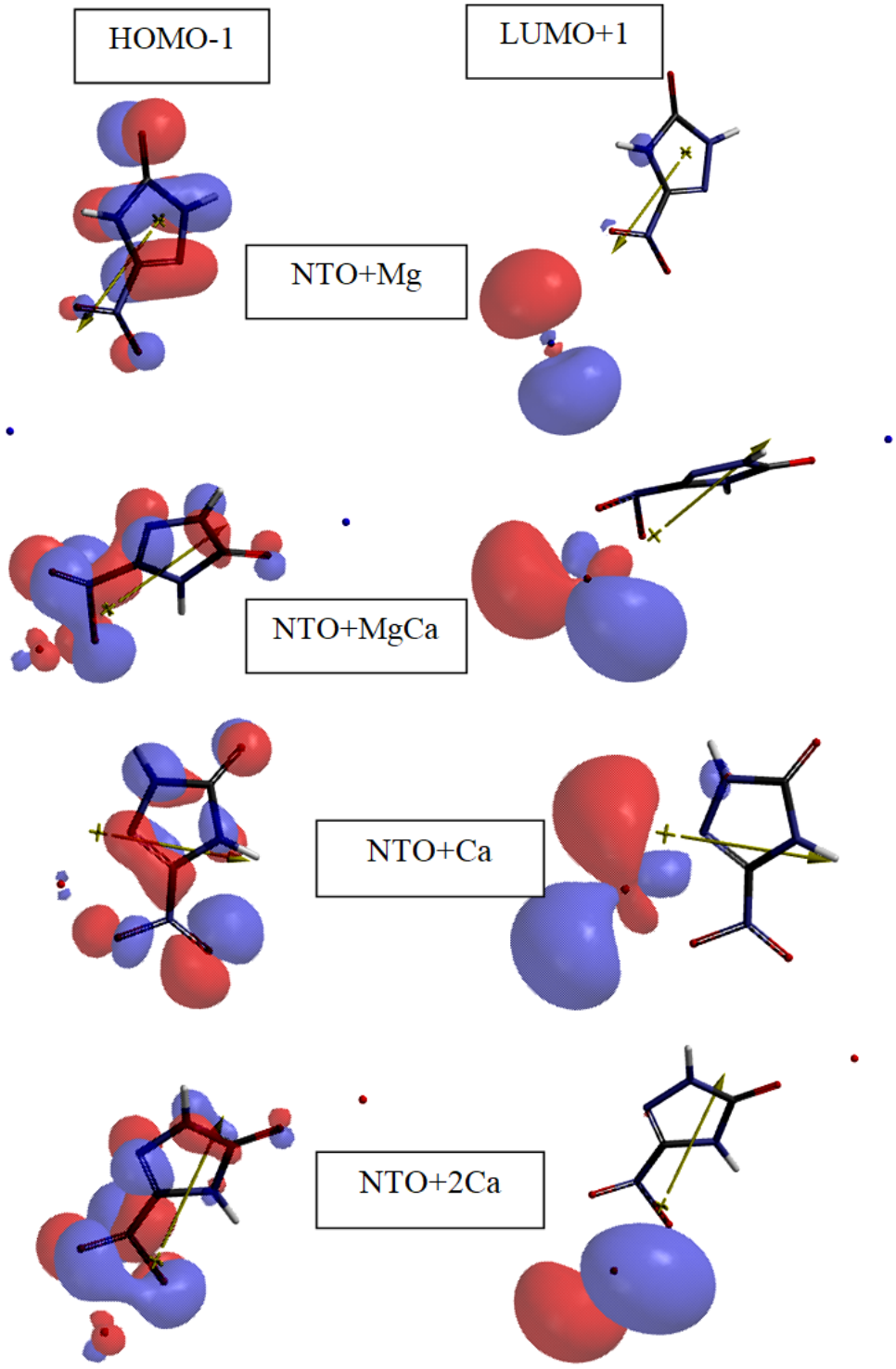

Figure 8. The HOMO and LUMO patterns of the composites considered.

Composite NTO+Ca is characterized with minute contribution of the calcium into the HOMO, contrary to its huge contribution to the LUMO. In NTO+2Ca case the great contribution to the HOMO comes from the calcium atom which is nearby the carbonyl moiety of NTO whereas the calcium atom next to the nitro group is the main contributor of the LUMO.

Figure 9 displays the HOMO-1 and LUMO+1 patterns of the composite systems. In all the cases contribution of the metal is nothing or very minute to the HOMO which is not the case in the LUMO of the composite.

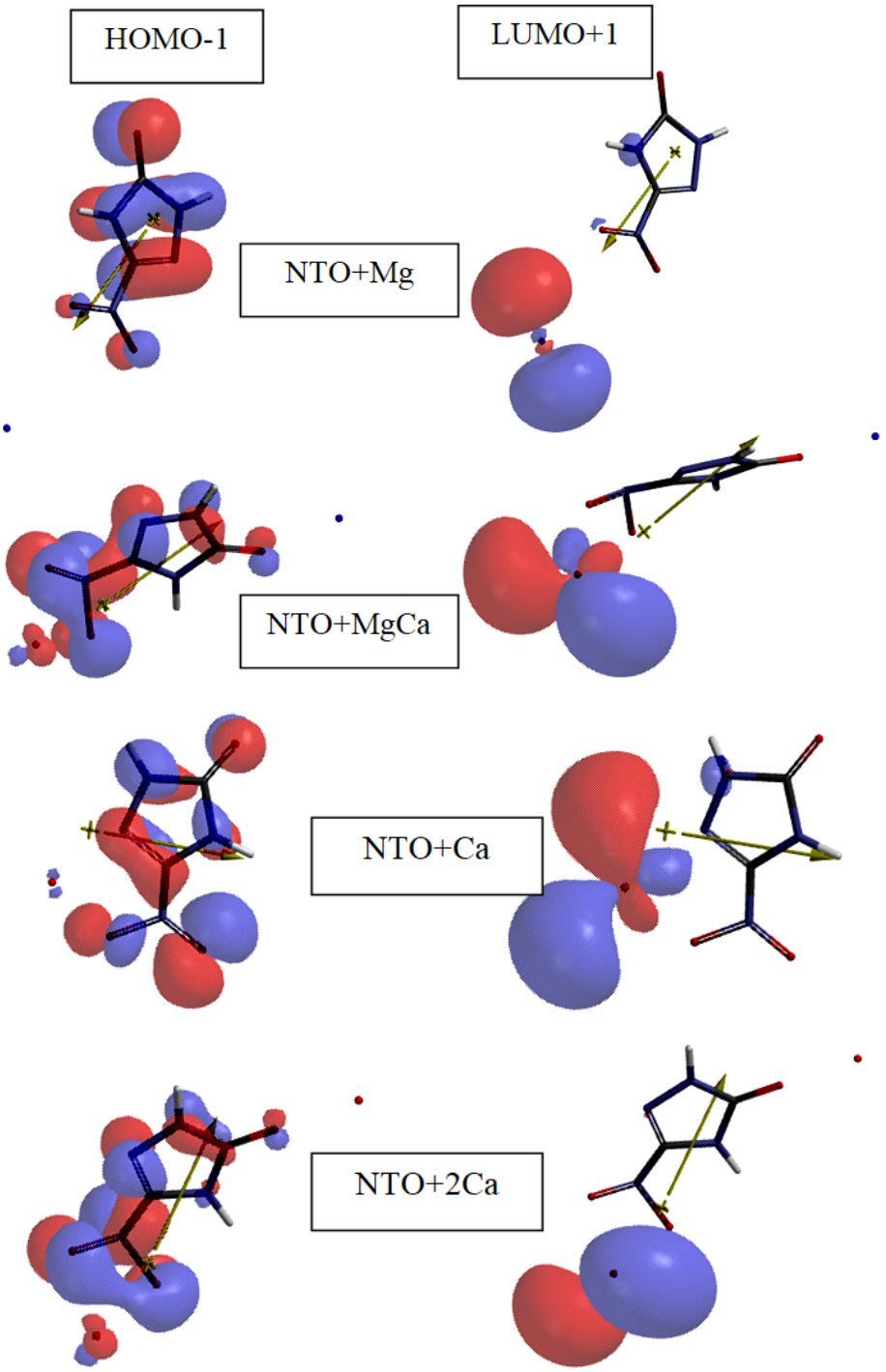

Figure 9. The NEXTHOMO and NEXTLUMO patterns of the composites considered.

Figure 10 shows the calculated UV-VIS spectra (time dependent, TDDFT) of the composites considered. As seen in the figure, NTO+Mg spectrum is confined into the UV region but the UV-VIS spectra shift to higher wavelengths as the calcium content increases in the composites.

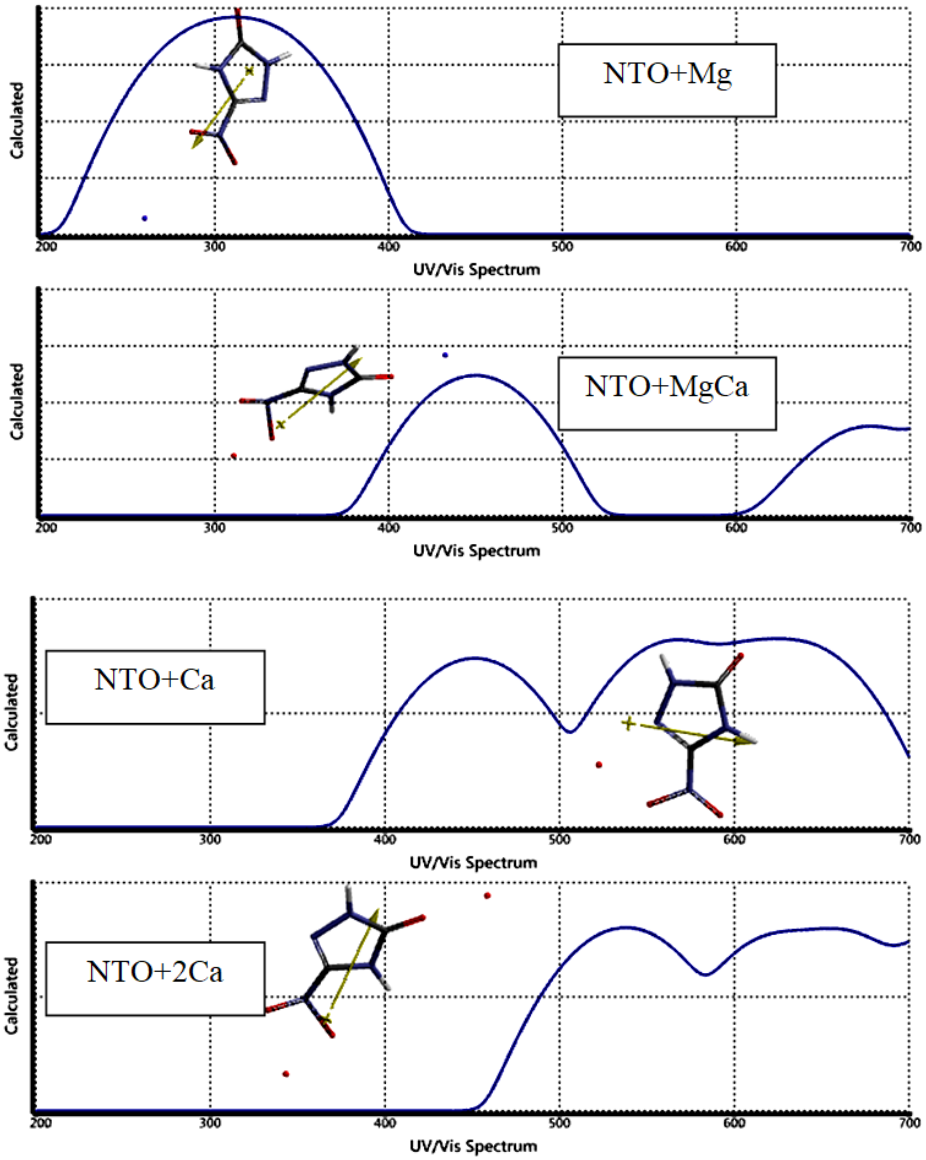

Figure 10. The UV-VIS spectra of the composites considered.

Table 5 shows the main absorption peaks of the composites. Since the calculated spectra involve not only the HOMO-LUMO excitations, some of the spectra possess shoulders or overlapped peaks. The calculated intensities of the peaks are related to magnitudes of the transition moments between the orbitals involved which vary from composite to composite [35,36].

Table 5. Main absorption peaks (nm) of the composites.

NTO+Mg	NTO+MgCa	NTO+Ca	NTO+2Ca
322.95	450.10	451.14	637.85
	650.02	566.29	660.12
	774.42	637.07	755.91

4. Conclusion

The present computational study has focused on the interaction of Mg or/and Ca atom(s) and the well known explosive, NTO within the restrictions of DFT and the basis set employed. Both of the metals considered mainly affect the electron distribution of the organic component, NTO while they acquire some positive charge in all the cases. The structural or conformational perturbations caused by the metals are less. The UV-VIS spectra of the composites exhibit great bathochromic effect as the calcium content increases. Among the composites, NTO+MgCa possesses the narrowest interfrontier molecular orbital energy gap value followed by NTO+2Ca. Thus, they might find some applicability for modifying some ballistic properties of NTO.

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