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Effect of magnesium or/and titanium on NTO molecule – A DFT study

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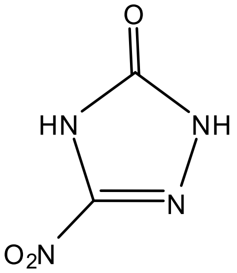
Abstract

Magnesium or/and titanium composites of 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO) have been investigated within the restrictions of density functional theory at the levels of B3LYP/6-31++G(d,p) and 6-311++G(2df,2p). The results indicate that the composites considered are exothermic and favorable in terms of H° and G° values. Also they are electronically stable. Various structural, quantum chemical and spectral (IR and UV-VIS) data are collected and discussed. The metals in the structures of the composites acquire some partial positive charges, such that the titanium being more positive than the magnesium in each case. In some of the composites, titanium atom and the nitro group of NTO undergo a kind of complex formation.

1. Introduction

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



Various articles on NTO and its tautomers have been published [7-15]. Although, its explosive performance characteristics are similar to RDX, it has been observed that NTO is less sensitive [13]. NTO has captured a major role in research of energetic materials as one of the important insensitive high explosive. A key characteristic of the thermally stable NTO is its insensitivity to impact, friction, heat, spark and shock waves [14]. It is relatively easy to synthesize. It displays some performance characteristics comparable to those of the currently commonly employed secondary explosives and possesses an appropriate potential to be used as an explosive and propellant ingredient. This compound has been shown to be less harmful to human health than the traditional explosives [15]. It can be also pressed without a binder into desired morphology having a high density [16]. Several authors have tailored its particle size and morphology in order to meet the requirement of energetic materials formulations. Spherical morphology is revealed to be appropriate for better processability and has great impact on scale to alter the performance and insensitivity towards a sudden mechanical stimuli than non-spherical crystals [17,18]. However, this nitrogen heterocyclic energetic compound presents some

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drawbacks, which limit its further applications, such as negative oxygen balance, negative enthalpy of formation and acidity. To overcome such shortcomings, the researchers have adopted two main approaches. The first one concerns the preparation of NTO derivatives owing to its acidity and the second one is dedicated to 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 like Al, Mg etc., are often involved in formulation of certain ammunition to increase the heat output of the composite. The interaction of TATB and magnesium are investigated quantum chemically within the limitations of density functional theory (DFT) at the levels of B3LYP/6-311++G(d,p) level [20].

Titanium is used in fountain fireworks as admixture of various energetic materials [21]. The use of the pyrotechnic, titanium/potassium perchlorate ($Ti/KClO_4$), for hot wire actuation applications increased during the early 1970's as a response to the decision not to use primary explosives. $Ti/KClO_4$ is static sensitive in the bulk but there is reduced static sensitivity when loaded in a device. Also, its other sensitivity properties such as friction, impact and thermal ignition are significantly better than primary explosives. In 1974, it was found that the pyrotechnic mixture, titanium hydride/potassium perchlorate ($TiH_2/KClO_4$) was insensitive to initiation from an equivalent human body discharge. This electrostatic discharge (ESD) insensitivity included bulk, pressed and loaded forms of $TiH_2/KClO_4$. Subsequent ESD tests with $TiH_2/KClO_4$, using discharge voltages in excess of 40 kilovolts and no resistance in the ESD circuit have never initiated this pyrotechnic. Its upper voltage or energy for ESD ignition is not known [22].

Although, the transition metals of group IV are well known as potent pyrotechnic fuels, metal powders are susceptible to aging and pyrotechnic compositions containing them can be sensitive to unintended ignition by electrostatic discharge [23].

The effect of titanium on FOX-7 has been investigated at the molecular level within the constraints of density functional theory (DFT) [24]. In the present treatise, both the individual effects of magnesium and titanium and also their mutual effect on NTO molecule are considered within the restrictions of DFT 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 [25-27]. Afterwards, the structure optimizations have been achieved within the framework of Hartree-Fock and finally by using density functional theory (DFT) at the levels of B3LYP/6-31++G(d,p) and (partly) 6-311++G(2df,2p) [28,29]. 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 [30]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [31] and Lee, Yang, Parr (LYP) correlation correction functional [32]. 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 cleavage occurred or not during the geometry optimization process. All these computations were performed by using SPARTAN 06 program [33].

3. Results and Discussion

Formulation of energetic materials sometimes include certain metals like aluminum, magnesium, zinc etc., just to improve some properties of them, such as heat outputs [34].

Magnesium atom in its ground state has the electronic configuration of $1s^22s^22p^63s^2$ whereas titanium possesses $[Mg]3p^63d^24s^2$ having some empty d-atomic orbitals, such as 3d and 4d [35].

Figure 1 stands for the optimized structures of the composites considered. The figure also displays the direction of the dipole moment. It is to be noted that in the case of B3LYP/6-311++G(2df,2p) level of calculations, vibrational frequencies could not be obtained due to the incapability of the program. Thus, certain quantum chemical data are missing for that level of calculations. For the ternary composite, NTO+Mg+Ti, two minima have been obtained (structures III and IV) which implies rather rough potential energy surface for the ternary composite, however structure IV is more favorable and stable than its isomer-III (see below paragraphs). While the optimization process at the B3LYP/6-311++G(2df,2p) level, only structure-IV was obtained. As seen in the figure the magnesium atom in all of the cases prefers nearby the carbonyl oxygen atom. The distance between them is 2.785, 2.055 and 2.334 Å, respectively in I, III and IV. Also note that whenever titanium atom participate (except III) the NO_2 group is out of plane of the ring and inclines towards the titanium atom.

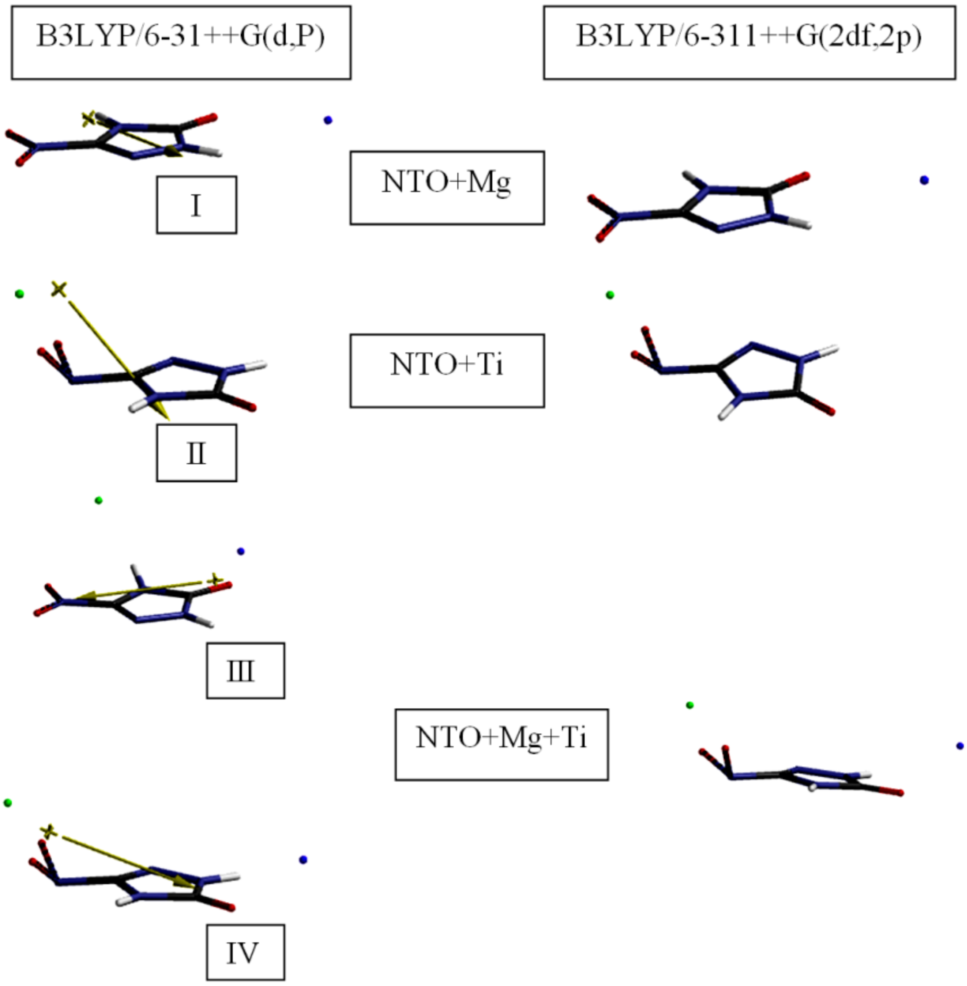


Figure 1. Optimized structures of the composites considered.

Table 1 lists some values for the composites considered and Table 2 shows some thermo chemical properties of them.

Table 1. Some values for the composites considered.

No	Composite	Formula	MW (amu)
I	NTO+Mg	$C_2H_2N_4O_3$.Mg	154.368
II	NTO+Ti	$C_2H_2N_4O_3$.Ti	177.943
III	NTO+Mg+Ti	$C_2H_2N_4O_3$.Mg.Ti	202.248
IV	NTO+Mg+Ti	$C_2H_2N_4O_3$.Mg.Ti	202.248

While the optimization process at the B3LYP/6-31++G(d,p) level, the first minimum for structure-III is obtained but persistent search resulted in another one, IV, which is more stable than III.

As seen in the table of standard thermo chemical formation data of the species considered (Table 2) all the composites are exothermic (H° values) and they are favored according to their G° (Gibbs free energy of formation) values. Composite-IV is more exothermic and more favorable than the isomeric ternary composite-III. Hence, the presence of Ti atom gives valuable contribution to H° and G° values.

Table 2. Some thermo chemical properties of the composites considered.

No	H°	S° (J/mol°)	G°
I	-1895660.921	374.68	-1895772.633
II	-3600471.686	373.25	-3600582.956
III	-4125421.816	406.67	-4125543.063
IV	-4125789.181	404.34	-4125909.718

Energies in kJ/mol. B3LYP/6-31++G(d,p) level.

Table 3 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 3. Some energies of the composites considered.

No	E	ZPE	E_C
I	-1895842.05	175.56	-1895666.49
II	-3600632.20	170.55	-3600461.65
III	-4125583.36	173.22	-4125410.14
IV	-4125949.37	171.64	-4125777.73

Energies in kJ/mol. B3LYP/6-31++G(d,p) level.

Figure 2 shows ESP charges on atoms of the composites considered. Note that 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 [33].

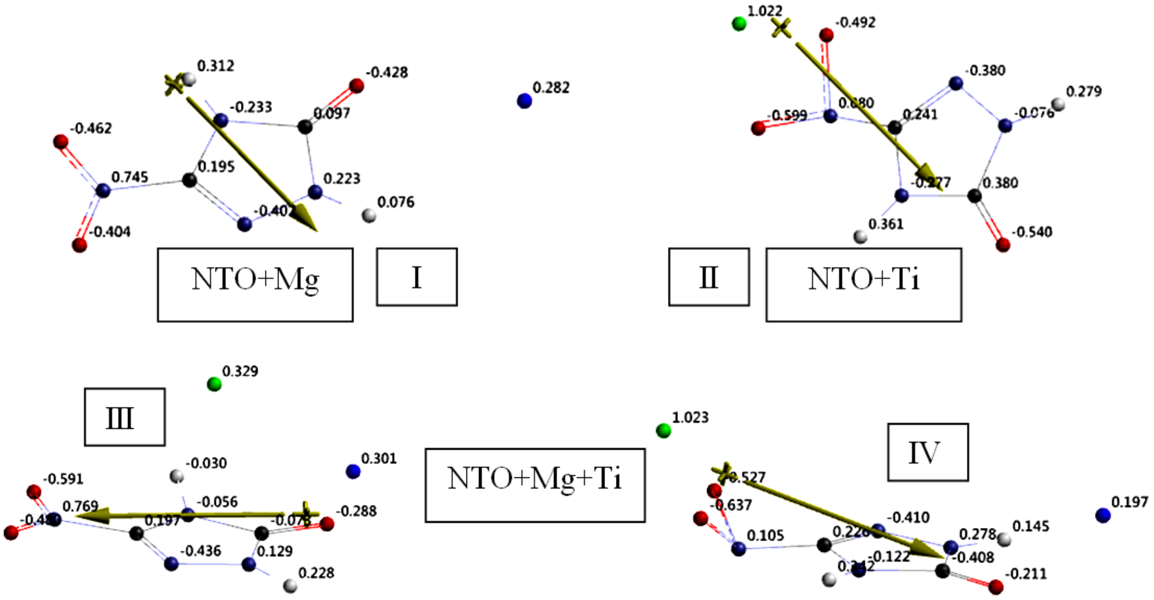


Figure 2. ESP charges on atoms of the composites considered.

Figure 3 displays the variation of the CFD centers of the composites considered (Green: HBA; Blue: Hydrophobe; Purple: HBA and/or HBD and +ionizable). HBA and HBD refer hydrogen bond acceptor and donor, respectively.

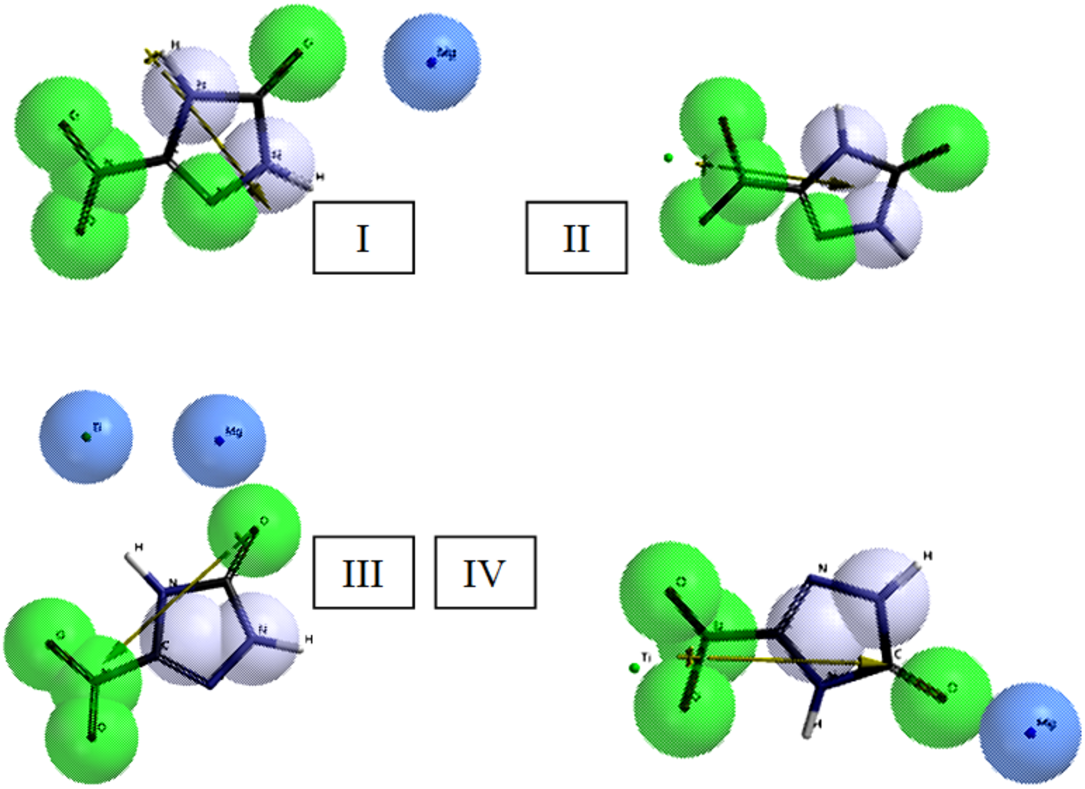


Figure 3. Variation of the CFD centers of the composites considered.

ESP maps of the composites considered are displayed in Figure 4 where negative potential regions reside on red/reddish and positive ones on blue/bluish parts of the maps.

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

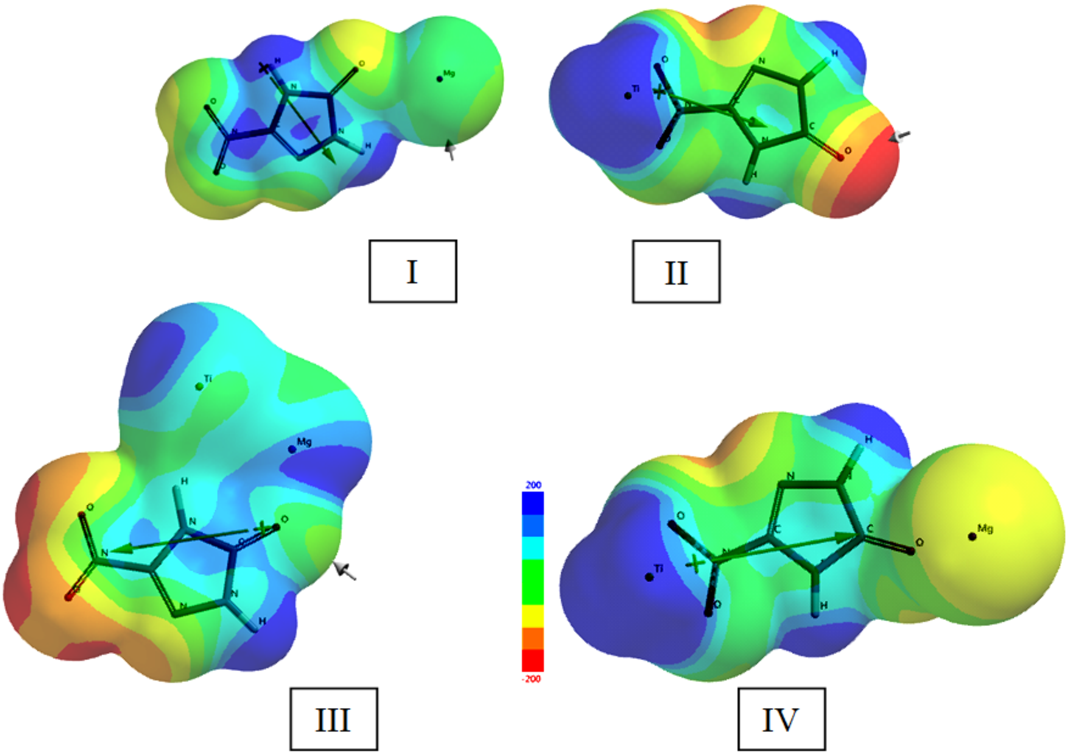
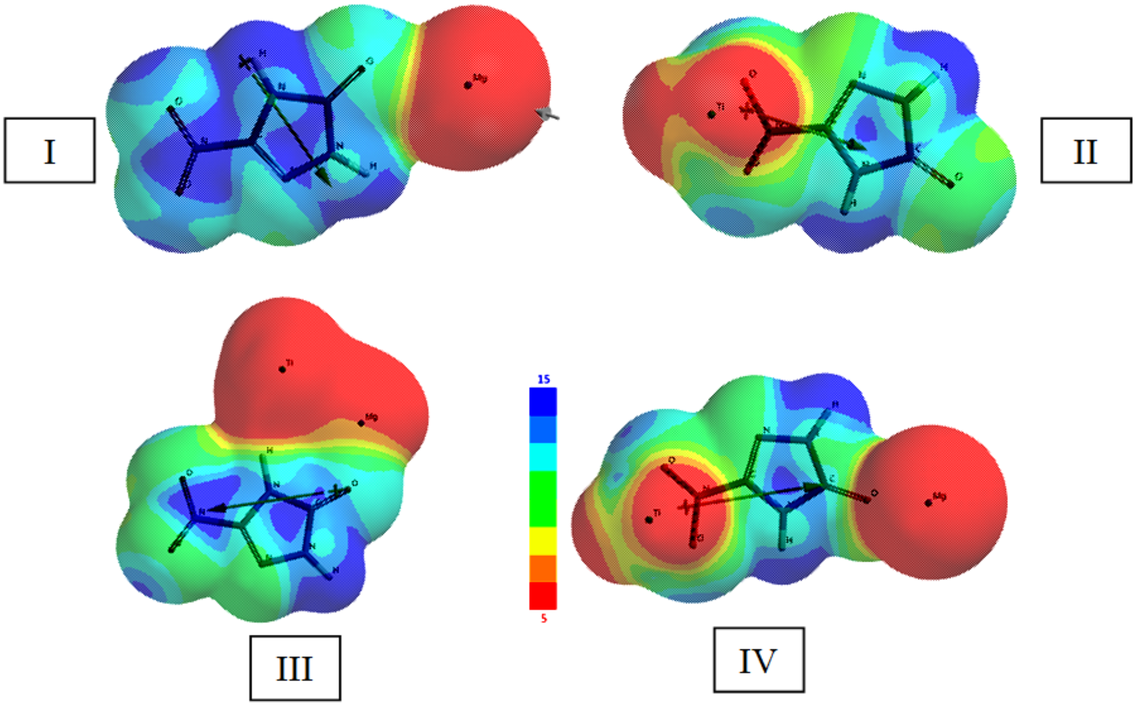


Figure 4. ESP maps of the composites considered.



.**Figure 5.** The local ionization maps of the composites considered.

Figure 6 shows the LUMO maps of the composites considered. 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 of the attack of nucleophiles [33]. Positions where the greatest LUMO coefficient exists is the most vulnerable site in nucleophilic reactions.

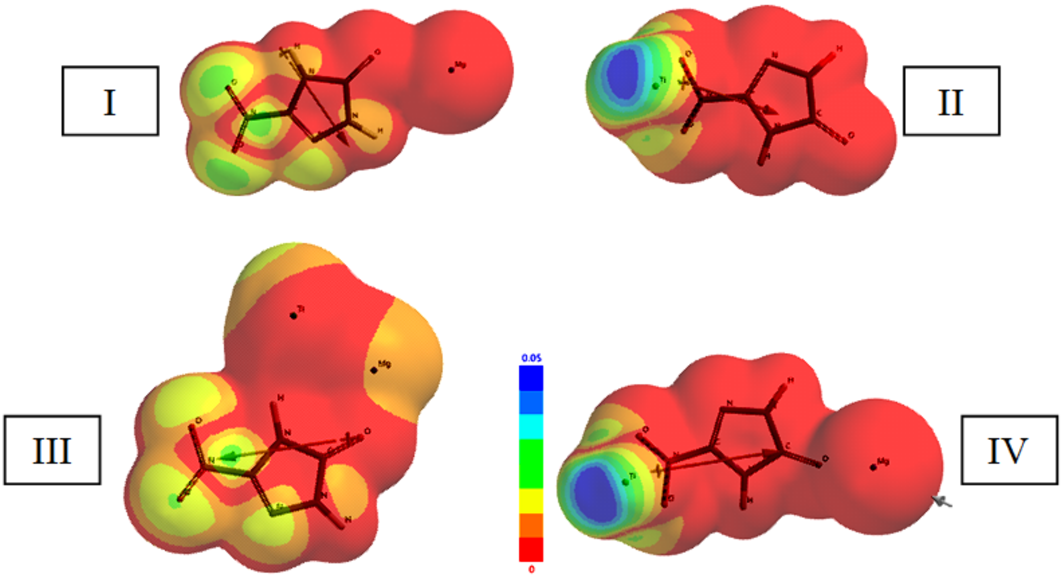


Figure 6. The LUMO maps of the composites considered.

Figure 7 shows the bond densities of the composites considered. Note the interaction of the titanium atom with the oxygens of the nitro group in composites II and IV that the bond density there is appreciable.

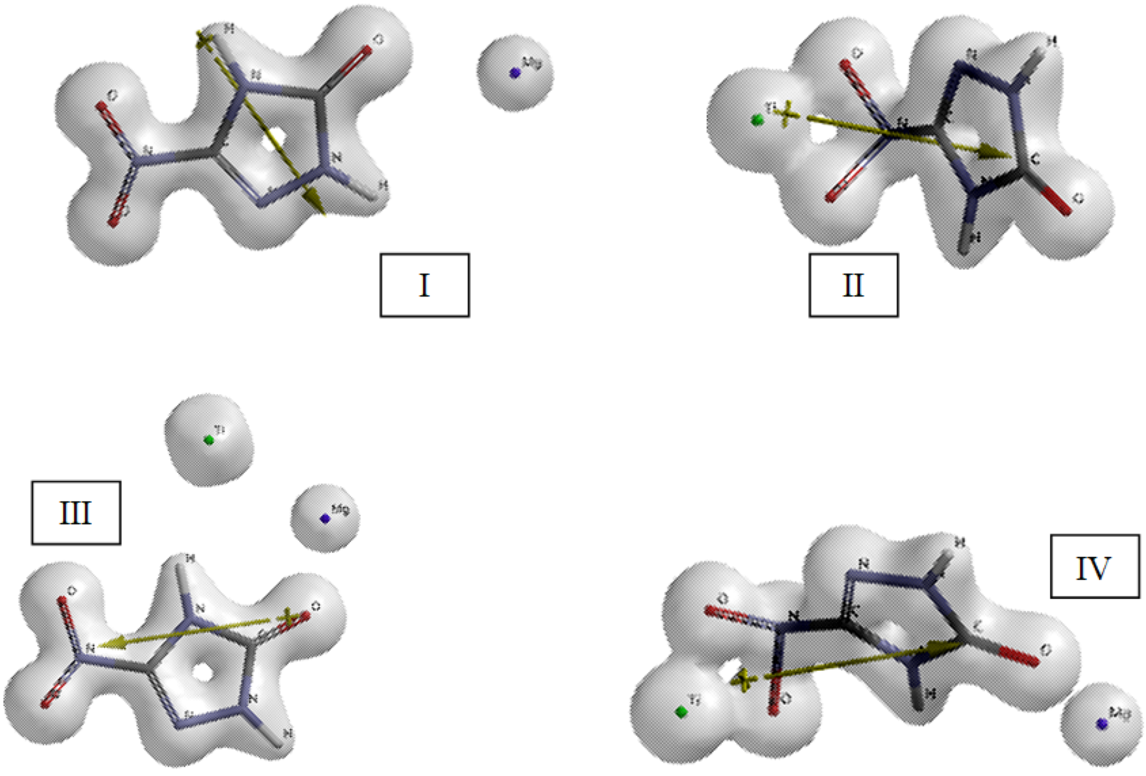


Figure 7. The bond densities of the composites considered.

Some of the orbital energy levels of the composites systems considered are shown in Figure 8. It is to be mentioned that the inner lying molecular orbitals are assumed to be responsible for the thermal stability. The figure shows that titanium atom lowers the HOMO energy level but raises up the LUMO as compared to magnesium atom (composites I and II). Note that Pauling electro negativities of Mg and Ti are 1.2 and 1.5, respectively [36]. Also the NEXTHOMO and NEXTLUMO energy levels are raised up by the titanium atom. As for the composites III and IV, thus a narrowing of interfrontier molecular orbital energy gap happens in IV compared to III (see also Figure 7 for relevant bond density maps).

Table 4 shows the HOMO, LUMO energies and Δε ($\Delta\varepsilon = \varepsilon_{LUMO}\text{-}\varepsilon_{HOMO}$) values of the composites considered. The algebraic orders of the HOMO and LUMO energies are II<I<IV<III and I<IV<II<III, respectively. Thus, the interfrontier molecular orbital energy gap values, constitute the order of IV<III<I<II.

Figure 9 displays the HOMO and LUMO patters, whereas the NextHOMO (NHOMO) and NextLUMO (NLUMO) patters of the composites systems considered are shown in Figure 10.

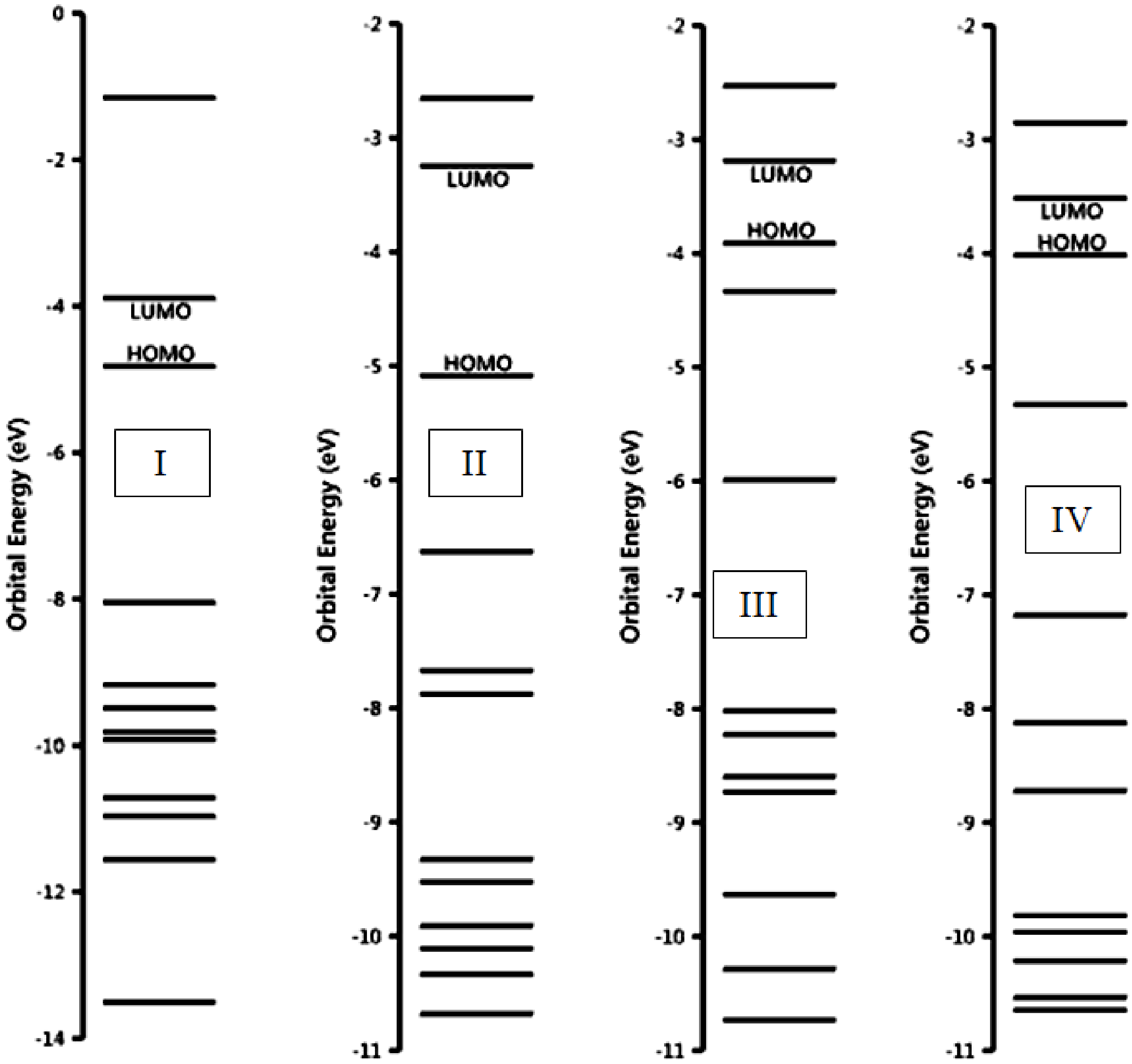


Figure 8. Some of the orbital energy levels of the composite systems considered.

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

Composites	HOMO	LUMO	Δε
I	-464.93	-375.38	89.55
II	-490.73	-313.28	177.45
III	-376.96	-307.78	69.18
IV	-387.31	-338.85	48.46

Energies in kJ/mol. B3LYP/6-31++G(d,p) level.

As seen in Figure 9, in composite-I the HOMO is mainly constructed by the magnesium atom having a spherical shape whereas it contributes nothing to the LUMO which exhibits a π-symmetry over the organic partner. In the case of composite-II, the titanium atom is the only contributor of the HOMO whereas the LUMO spreads over almost the whole of the composite. As for composite-III, both of the frontier molecular orbitals are constructed by all the atoms except some hydrogens and a little contribution comes from the magnesium atom. In the case of IV, the HOMO is constructed mainly by the magnesium, the contribution of the titanium is considerably much smaller. Whereas in the LUMO, the magnesium atom and some atoms of NTO do not participate at all.

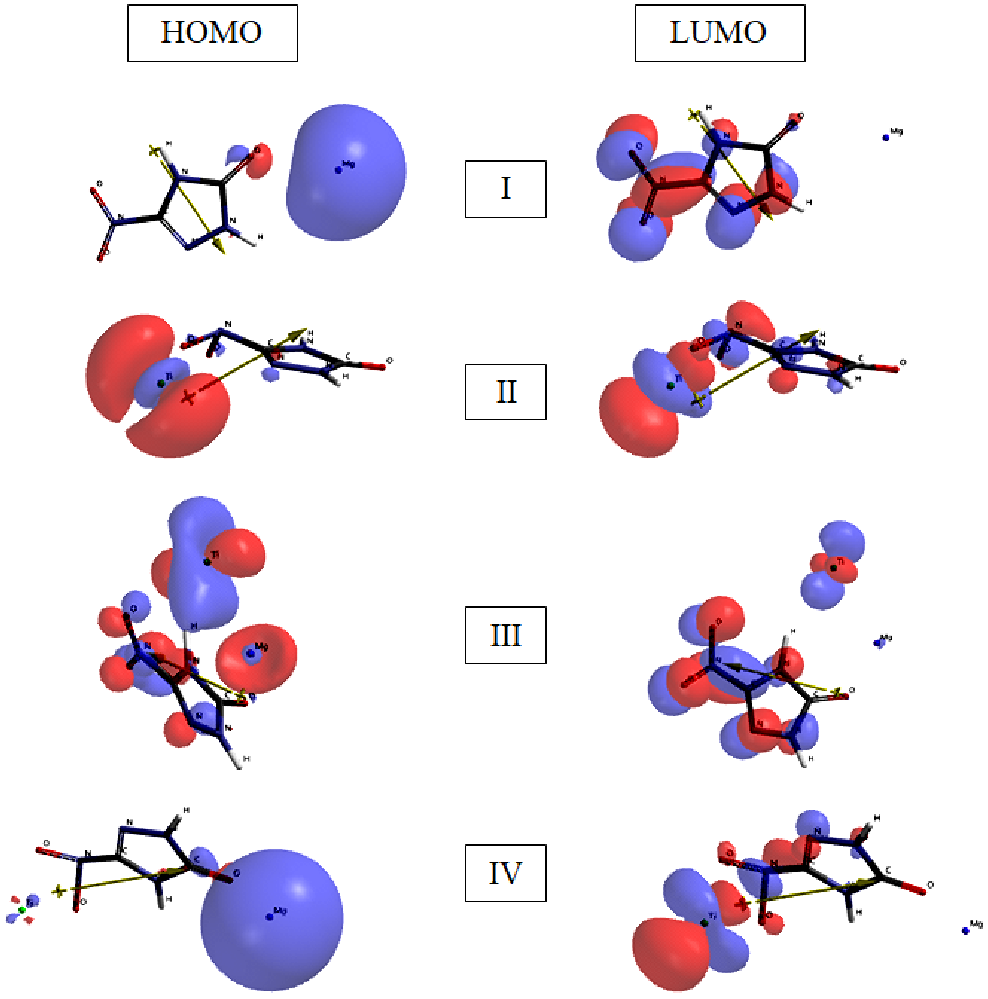


Figure 9. The HOMO and LUMO patters of the composite systems considered.

Note that in the case of composites III and IV, main contributors to the NEXTHOMO and NEXTLUMO (NEXTHOMO, NEXTLUMO are HOMO-1 and LUMO+1, respectively) are the inorganic partners (Figure 10).

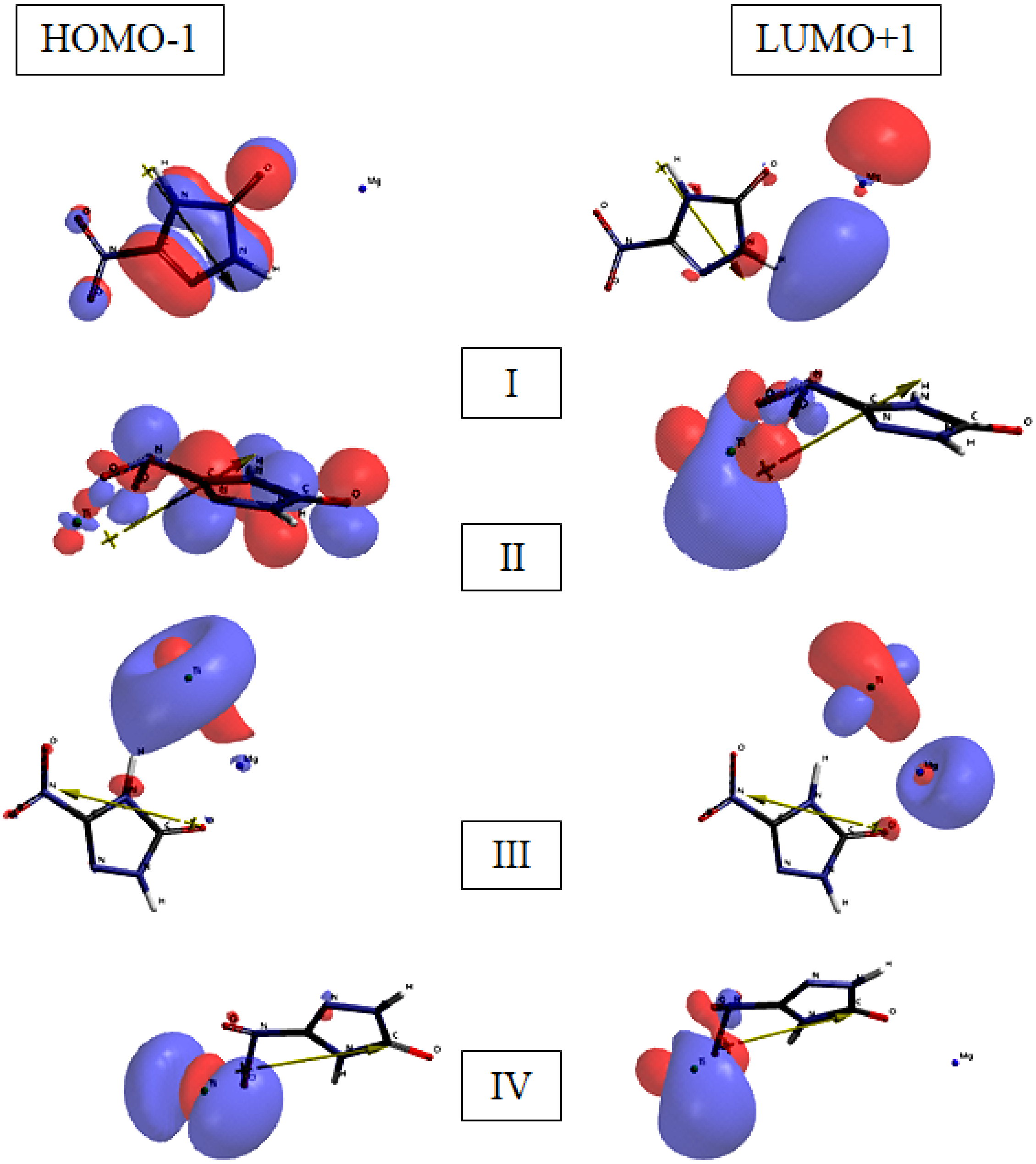


Figure 10. The NEXTHOMO and NEXTLUMO patters of the composite systems considered.

Figure 11 shows the calculated IR spectra of the composites considered. The peak(s) at 3700-3500 cm^{-1} belong to N-H stretching vibration(s) in all the composites. However, composite-III has N-H stretching vibrations at 3658 cm^{-1} and 2806 cm^{-1}. The lower one is rather unexpected and stands for N-H which is nearby the titanium atom. Although, the Ti and NH distance is about 2.7 Å, the presence of the metal atom has a paramount effect. Composit-IV has two closely located N-H vibrations 3675 cm^{-1} and 3665 cm^{-1} in the expected region for N-H stretchings. In all the spectra the sharp peak in the range of 1700-1800 cm^{-1} is moslyt the (imide) carbonyl stretching which occurs at 1808, 1822, 1694 (very weak), and 1746 cm^{-1} for composites I-IV, respectively. They are overlapped with N-H bendings and skeletal breathing of the ring. The peaks at 1400-1650 cm^{-1} stand for C-NO$_2$ and N-O stretchings.

Figure 12 shows the calculated UV-VIS spectra of some of the composites considered (I and II). On the other hand, composites III and IV do not have any absorption peaks in the range of 200-700 nm. However, from comparison of spectrums of I and II one can realize that titanium appreciably shifts the peaks into the visible region. Probably, because of the combine effects of the metals considered, composites III and IV are out of the sight in the above mentioned range.

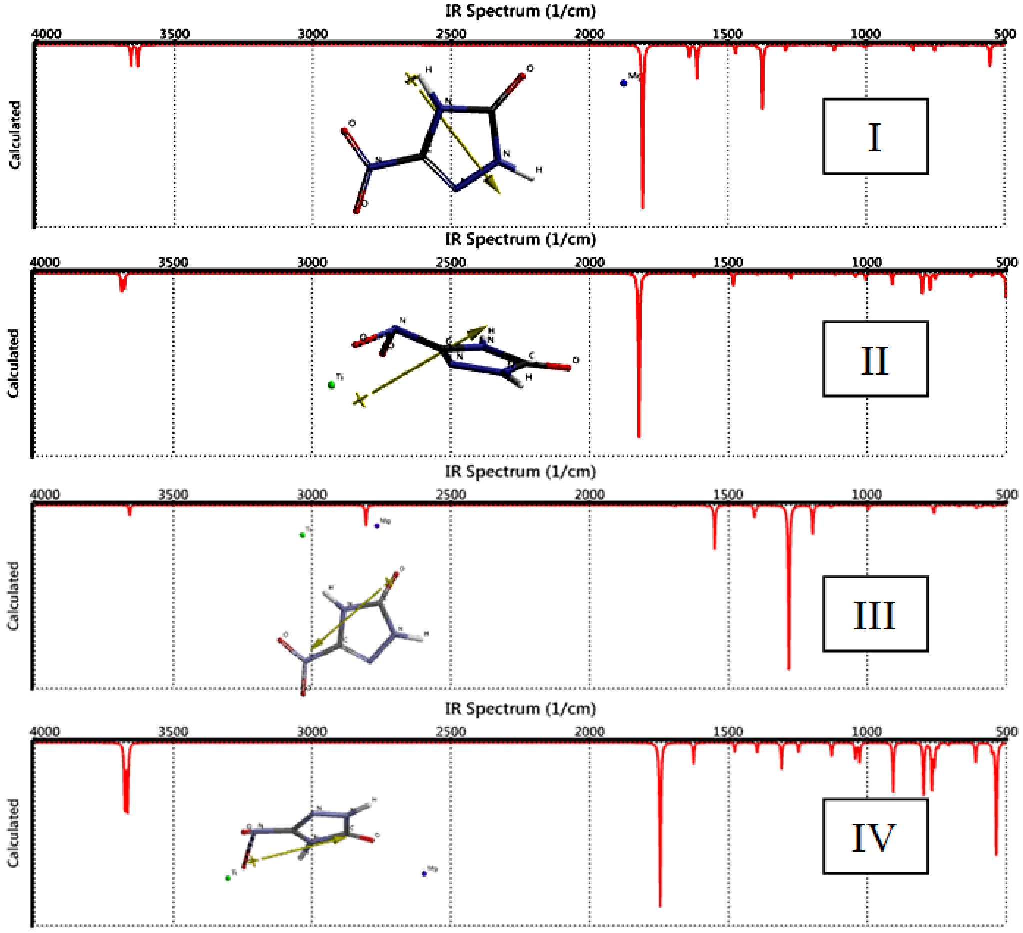


Figure 11. The calculated IR spectra of the composites considered.

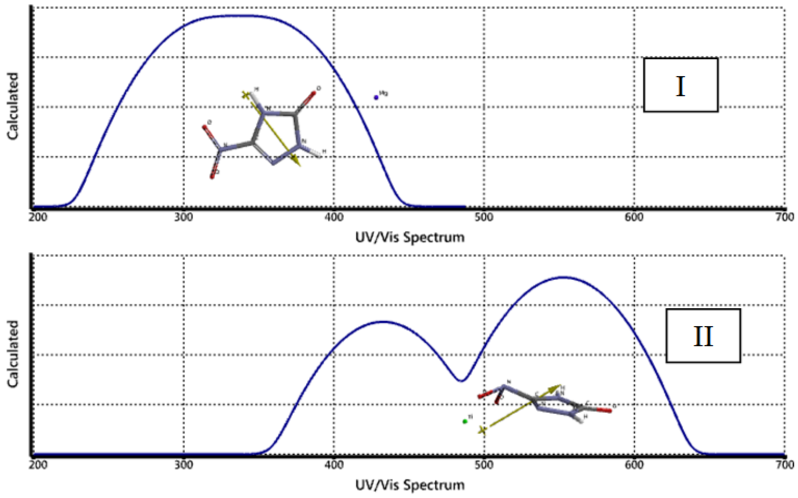


Figure 12. The calculated UV-VIS spectra of the composites considered.

4. Conclusion

The present study, performed on the magnesium or/and titanium composites of NTO within the restrictions of density functional theory has revealed that they are thermally favorable and electronically stable in the vacuum conditions. However, the metals considered somewhat perturb the parent structure in each composite, by transferring some electron population to the organic component, acquiring some positive charge itself/themselves. In that sense titanium is more effective than magnesium. On the other hand, the frontier molecular orbital energy levels are effected depending on the kind of the metal atom involved in the composite. Some of them are lowered or raised in energy. The most effective narrowing of interfrontier molecular orbital energy gap happens in the case of composite-IV arising from the combined effects of Mg and Ti atoms. Thus, the composite should have some peculiar properties, one of which is its UV-VIS spectrum which shows strong bathochromic effect so that probably it absorbs in the IR region. Its technical applications have to be investigated.

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