UNIVERSITY BABEŞ-BOLYAI
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PHD THESIS

Light-induced phenomena in molecular complexes

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Contents

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The interaction of the electromagnetic radiation with molecular systems

The interaction of the electromagnetic radiation in the ultraviolet and visible region (UV-Vis: 100 –700 nm) with different molecular systems induces various effects at their electronic levels. The UV-Vis light is mainly considered as a non-ionizing radiation which, instead of generating charged ions when passing through matter, has enough energy to excite the molecular valence electrons. However, these excitations could initiate several molecular processes (photoionization, predissociation, photodissociation or chemical reactions), which, for example, could cause direct DNA damage in the cell[1]. The destructive action of the UV-Vis radiation has a wide range of biological and medical applications, like photo-chemotherapy, sterilization, air purification or food processing. The UV-Vis radiation under well-chosen radiation conditions (wavelength, intensity, exposure time, etc.) can be used not just for killing cancerous cells or unwanted microorganisms (by deteriorating their genetic material), but also to induce more complicated biological or chemical phenomena. Nowadays, there is a growing need to develop new smart or meta-materials with different specific functionalities which can be changed in a controlled manner by external stimuli, like temperature or electromagnetic field[2–4]. A very interesting class of systems are the photovoltaic materials, which directly convert solar energy into electricity, and are based on the creation of electron-hole pairs induced by an external electromagnetic radiation and the generation of the current or power by separation of the different charge carriers created after excitation. Another promising class of materials is represented by supramolecular systems which presents the so-called spin crossover (SCO) behavior (transition between ”Low” spin (LS) and ”High” spin (HS) electronic states)[5]. Although the most experimental studies focus on the thermal activation of the LS $\leftrightarrow$ HS transition[6,7], there are several attempts to use laser irradiation for inducing spin switches[8–13].

Quantum chemical modeling of electronically-excited molecular systems provides information on different processes occurring in excited states (vertical and adiabatic excitations, geometry relaxation, ultrafast decay through conical intersection or intersystem crossing). The systems of interest are typically large complexes of 50-60 atoms, built around a central transition metal atom and the octahedral ligand structure. It is hardly possible to treat them using sophisticated multireference methods, due to the need of considering large computational resources. An alternative theoretical framework used to study these molecular complexes is to apply the density functional theory (DFT)[14,15] and its linear response time-dependent (TD-DFT)[16,17] methods, which can handle moderately large ($\approx 50 - 70$) number of atoms. The key for an accurate description of these complex systems is to use high performance exchange-correlation (XC) functionals[18–20], which cover, for example, electron delocalization effects, charge transfer- and Rydberg-excitation, etc.

This work aims to impact topical areas of physical chemistry and chemical physics. The developed methodologies and tools are expected to result in more accurate predictions of the controlled behavior and response in the case of electron transfer processes in donor-acceptor complexes and of the interaction with coherent pulsed UV light for different spin crossover molecular complexes. Accordingly, we will be able to gain a deeper understanding of the following aspects: (a) the photo-induced electron transfer (ET) in systems based on bulk heterojunctions; (b) the necessary conditions (efficient absorption, proper spectral domain for the laser excitation, good structural stability of the LS and HS configurations, etc.) needed for obtaining well-functioning spin crossover systems; (c) the basic theoretical principles of laser induced spin transitions; and (d) the nature of electronic excited states involved in the LS $\leftrightarrow$ HS transition. It is expected that, the present work will contribute: in the design process of donor-acceptor complexes, of interest for photovoltaic systems based on bulk heterojunctions; to the efficient design of a precise, robust, and reproducible laser-assisted spin crossover molecular complexes and to propose new solutions for polymers with unusual behavior, like breathing structure, considering the special property of the ligand bond variation with respect of the ”low” and ”high” spin states.

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Electron transfer in donor-acceptor systems

The space sampling of the relative equilibrium positions of the donor-acceptor configurations is a process that leads to a slow convergence for any optimization approach. This is due to the presence of quasi-equipotential regions in a system showing van der Waals interactions. This behavior was also present in our system composed of C_{70} as acceptor and Tris[4-(2-thienyl)phenyl]amine $(C_{30}H_{21}NS_3)$ as donor[21].

For the initial geometry configurations we selected five representative donor-acceptor structures realized by placing the $\mathrm{NC_3}$-group of the donor parallel and centered over a particular hexagon/pentagon of the acceptor at a 4 Å distance. The optimization of the complex was based on separate optimizations for the donor and acceptor fragments. The resulting geometric configurations are presented in Fig. 2.1. The optimizations lead to a change in the donor-acceptor distances by only 0.2 Å, the projection of the donor's N atom shifting towards the carbon vertices of the acceptor's facing hexagon or pentagon.

For each donor-acceptor configuration, three single-point calculations were performed in order to provide the detailed data required for the time evolution formalism (described in the previous section). Two single-point calculations were performed for the separate acceptor and donor parts in the distorted equilibrium configurations within the complex, and the third calculation was performed for the entire donor-acceptor system.

It can be noted that the LUMO level of the acceptor corresponds to the LUMO level of the entire complex, and the HOMO level for the separated donor part corresponds to the HOMO of the entire donor-acceptor compound. Figure 2.2 presents the HOMO and LUMO orbitals for the separated

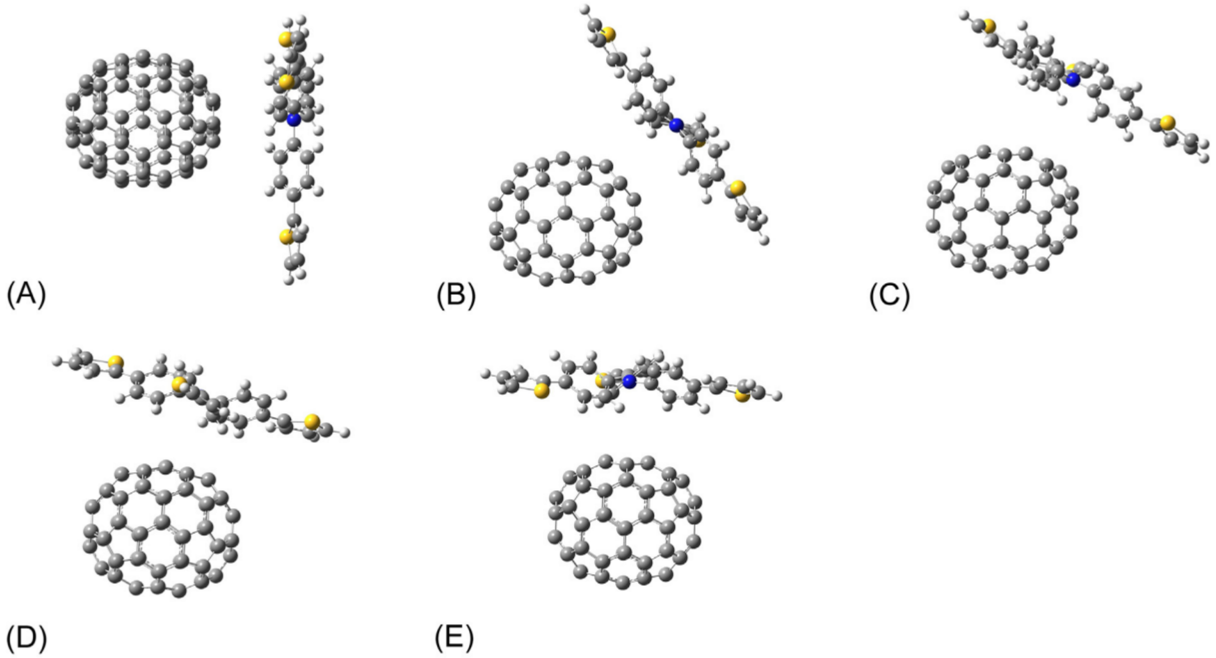

Figure 2.1. Equilibrium configurations of the donor-acceptor system.

acceptor and donor parts, as well as for the entire donor-acceptor complex. The HOMO orbital of the separated donor part is quite similar to the HOMO orbital of the donor-acceptor complex, while the LUMO orbital of the separated acceptor part matched with the LUMO orbital of the entire compound.

For the electron transfer calculations, four Gaussian pulses combinations were chosen for all five donor-acceptor configurations:
-P0 with a frequency of 0.63 PHz corresponding to a wavelength of 475 nm and a duration of 5 fs
-P1 with a frequency of 1 PHz corresponding to a wavelength of 300 nm and a duration of 5 fs
-P2 with a frequency of 2 PHz corresponding to a wavelength of 150 nm and a duration of 2.5 fs
-P3 with a frequency of 2 PHz corresponding to a wavelength of 150 nm and a duration of 5 fs

In Fig 2.3 the time evolution of the electron transfer for all A-E donor-acceptor configurations is presented, using the P1 pulse scheme. The electron transfer is defined by the difference of the instantaneous population of electrons and the number of nominal static electrons for the acceptor and for the donor, respectively. It can be observed that the electron transfers for the acceptor and donor show opposite sign and compensate each other in all five configurations.

Initially, the appearance of an inverse electron transfer from the acceptor to the donor can be seen, then after the termination of the pulse, an effective electron transfer from the donor to acceptor

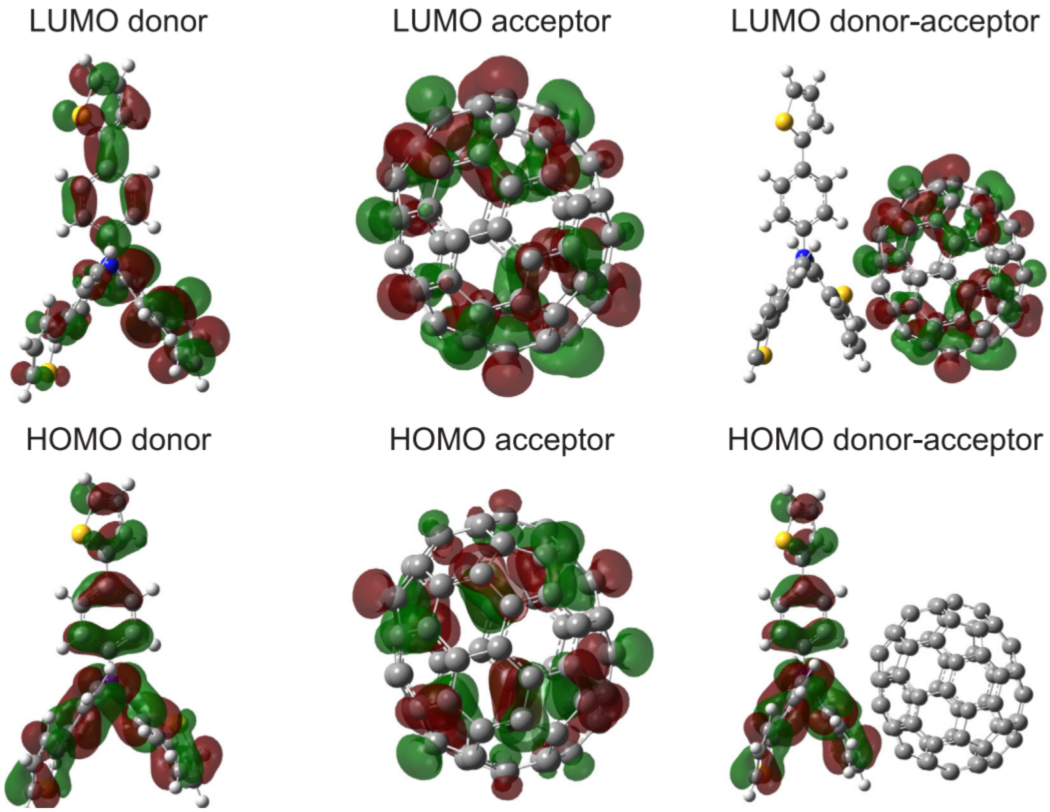

Figure 2.2. HOMO and LUMO orbitals (donor, acceptor and configuration C of the donor-acceptor system).

can be observed. In the case of P1 pulse, the maximum amount of electron transfer is around 2e, for all five donor-acceptor configurations. This result is promising from an experimental point of view.

The electron transfer was simulated for five different configuration setups of donor-acceptor pairs for a time span of 20 fs. Table 2.1 contains the results regarding the average electron transfer for configurations A-E. The results show an increase of the electron transfer for a longer duration of the pulse and for a frequency located in the resonant range. The maximum is obtained for the P3 pulse. The pulse P0 favors a particular behavior resulting in an inverse electron transfer of -0.285e in the case of configuration A (see Table 2.1). However it shows an efficient transfer of 2.198e in the case of configuration D. When the same pulse type is applied, the structural difference between configurations provides large differences in the process of electron transfer. Analyzing the results provided by the pulse P1, the maximum electron transfer is 1.842e for configuration C, while for the pulse P3 the maximum value of the electron transfer is 2.691e, reached for configuration D. The pulse P3 shows for all the configurations a value of the electron transfer over 2.1e, except the

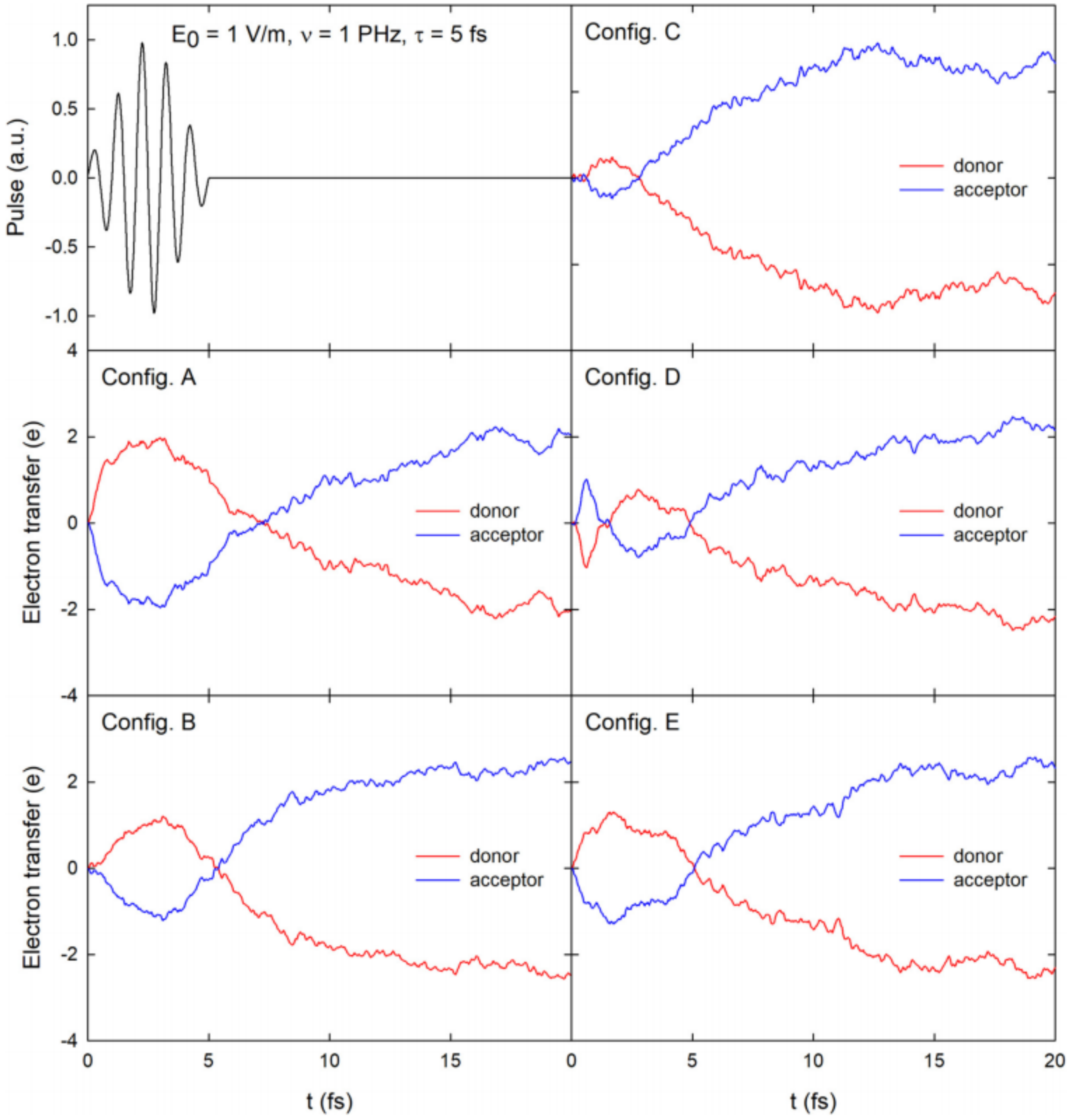

Figure 2.3. Electron transfer for the A-E configurations, under the influence of a pulse of electric field $E_0 = 1V/m$, frequency ν = 1 PHz, and duration t = 5 fs.

configuration B, with a transfer of only 1.699e.

In order to understand the processes of electron transfer, time-dependent calculations for the electronic populations were performed in the case of the donor-acceptor systems composed from the donor Tris[4-(2-thienyl)phenyl]amine($C_{30}H_{21}NS_3$) and the acceptor fullerene C_{70}. Five representative geometrical configurations of the donor-acceptor system were considered. The configurations present similar electronic structure, having the HOMO orbital of the donor-acceptor system localized on the HOMO of the donor, and with the LUMO orbital of the complex localized on the

Table 2.1. Average electron transfer for configurations A-E, for different frequencies ν (PHz) and duration t (fs) of the Gaussian pulse.

Conf.	ν	Electron transfer	
		$\tau = 2.5$	$\tau = 5$
A	0.63		-0.285
	1.00		0.448
	2.00	1.131	2.218
B	0.63		1.517
	1.00		1.195
	2.00	1.052	1.699
C	0.63		1.132
	1.00		1.842
	2.00	1.893	2.124
D	0.63		2.198
	1.00		1.135
	2.00	2.260	2.691
E	0.63		0.124
	1.00		1.060
	2.00	1.087	2.250

LUMO orbital of the acceptor part. The initial states for the Cayley's propagator time evolution formalism and the perturbed Hamiltonian were constructed starting from the molecular orbitals of the system and the initial time-independent Hamiltonian using Gaussian pulses.

The electronic populations dynamics were obtained using the Löwdin analysis. Using a time span of 20 fs, the average electron transfer occurring from the donor to the acceptor obtained was of two electrons. The electron transfer was improved by using pulse frequencies in the resonance domain of the system and also by increasing the duration of the applied pulse. The relevance of the geometrical displacement for all five configurations was underlined, and the lowest and highest electron transfers from the donor-acceptor configurations were identified.

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3

Spin transitions in spin-crossover systems

Nickel-porphyrins structures are used to investigate the coordination-induced spin crossover (CISCO) effect[1]. This is due to their rigid quadratic planar coordination. A spin transition is easily triggered by attaching a ligand to the metal center ion. In order for the transition to be reversible, the ligand must be designed in such a way that it can be switched between two states[2–4]. The magnetic bistability was experimentally investigated for the Ni–tetrakis(pentafluorophenyl)porphyrin (TPP) functionalized with a phenazopyridine (PAPy) arm (NiTPP-PAPY) complex by Venkataramani et al[5], which made it an ideal candidate for the study of the spin crossover phenomenon and the magnetic bistability under an induced laser perturbation. The experiments showed that when the complex is irradiated with a laser light of 500 nm, the total spin changes from the low state to the high state configuration. This is due to the changes induced by the phenoazopyridine(PAY) moiety in the nickel coordination sphere, the structure being modified from square planar geometry to square pyramidal[5,6]. The spin transition process presents reversibility for laser irradiation of 435nm, the interactions between PAPy and porphyrin having an important contribution in this transition process from one spin state to another.

The NiTPP-PAPY complex was investigated using different types of functionals: hybrid, meta-hybrid, and range-separated. The efficiency of each functional was tested computing the adiabatic singlet-triplet gap together with the singlet-triplet spin states conformations.

For the complex Ni-tetrakis porphyrin functionalized with a phenazopyridine arm, the adiabatic singlet-triplet energy gap and the Ni-N bond distance were investigated using several hybrid and meta-hybrid exchange-correlation functionals. Because of the multireference character methods (which include electron correlation effects), the functionals provide large differences in the singlet-triplet energy gap (of almost 1.5 eV) and in the metal-nitrogen bond distance (of 2.76 Å). It was observed that the dispersion correction effects have a strong influence over the Ni-N bond distance values; the large amount of HF exchange can influence the ligand bonds (because of the multireference character of the nickel 3d orbitals); the approximate density functionals do not remove the self-interaction errors completely. These deficiencies can be reduced by using a different mix of HF type exchange with DFT type exchange. From those 16 different exchange-correlation functionals, only the CAM-B3LYP-D, the ωB97XD, the M06, and the MN12-SX contains a proper mix of HF exchange with DFT exchange, in such way that the self-interaction errors are reduced. These functionals have included the dispersion corrections, which are shortening the metal-nitrogen bond distance, making the metal-ligand interaction stronger. In the case of NiTPP-PAPy complex, the strong metal-ligand interaction causes a larger charge transfer effect over the complex. In this way, the most appropriate functional, which can describe the spin-transitions in metal-organic complexes is the MN12-SX functional.

Considering the NiTP-biPAPy complex, in the singlet spin configuration, the S_7 electronic excitation facilitates the singlet to triplet spin transition. The S_7 excitation is a transition of n or π electron of the porphyrin ring to the π electrons of the phenazopyridine fragment arm, with an oscillator strength of 0.0262 obtained at 426 nm. In the case of the triplet configuration, T_{19} has an oscillator strength of 0.0028, large enough that the light is absorbed efficiently. T_{19} is a $\pi - \pi$ ligand-to-ligand charge transfer excitation type, obtained at 427.46 nm.

For investigating the spin transition mechanism and the effects of the charge transfer over the structural stability, two metal-organic complexes were considered: the porphyrin (P) and the diketopyrphyrin (DP) as planar ligands, together with the mesylate (Mes) as a vertical ligand. The singlet and triplet configurations of the two metal-organic structures (DP+Mes and P+Mes) were computed using B3LYP*-D3/def2-TZVP and CAM-B3LYP-17-D3/def2-TZVP levels of theory.

The graphics of the electrostatic potentials maps for both planar ligands were computed at the CAM-B3LYP-17-D3/def2-TZVP level of theory and are presented in Fig. 3.1.

The blue region of the DP ligand corresponds to the area with a larger deficit of electrons, where due to the negatively charged vertical ligand, a strong ionic interaction can be formed. Analyzing the porphyrin ligand, it can be seen that the electron-deficit region is much weaker, which leads to a smaller electrostatic attraction between the central ion and the vertical ligand.

The Natural Difference Orbitals (NDO) analysis provides a good view over the singlet-MECP-triplet transition. The NDO for the DP+Mes metal-organic complex was obtained at CAM-B3LYP17-

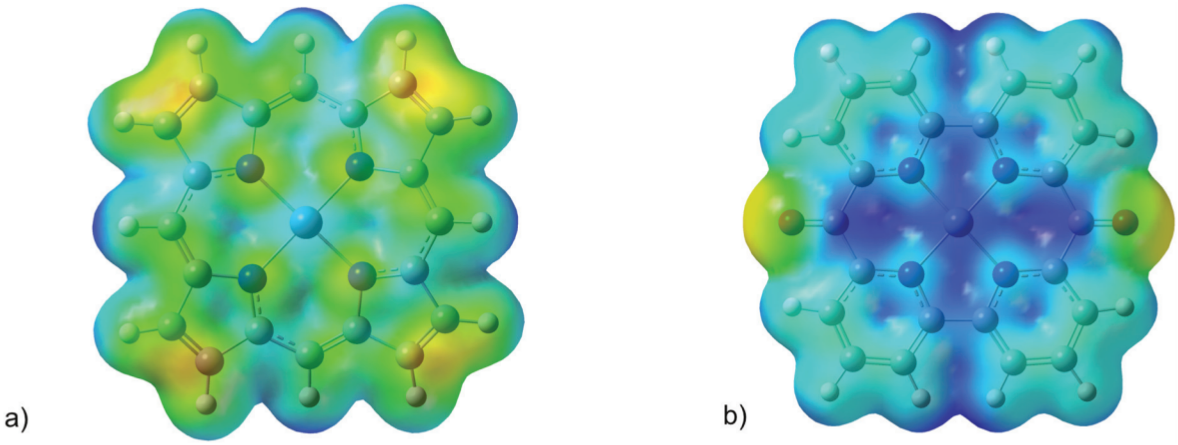


Figure 3.1. The electrostatic potential map around the porphyrin-type (a) and DP-type (b) planar ligand–Ni(II) complexes using E_{min} = +0.1e (red-yellow part) and E_{max} =+0.3e (dark blue part) charge values.

D3 level of theory. In the singlet equilibrium geometry the orbitals are located on the mesylate ligands and over the Ni atom from the planar ligand. Along the singlet to triplet transition, the orbitals are starting to migrate from the vertical ligand to the planar ligand. In the case of the singlet equilibrium geometry the molecular orbital configuration of the HOMO contains a combination of Ni(d_{z^2}) + O(sp^2) orbitals, while the triplet equilibrium geometry contains a combination of Ni(d_{z^2}) + O(sp^2) with Ni($d_{x^2-y^2}$) + σ orbitals. In the MECP state the contribution of the Ni(d_{z^2}) orbital is very small, because two electrons of the singlet HOMO move partially to Ni($d_{x^2-y^2}$) + σ and O(sp^2) + π orbitals. In the relaxation process the mesylate ligands move towards the central Ni atom, the π orbital becoming a d_{z^2} type (see Fig. 3.2).

For different metal-organic complexes, the role of porphyrin and diketo-pyrphyrine-based planar ligands was investigated in order to characterize the geometrical stability, the structural reversibility, and the appropriate excitation frequency domain. For these metal-organic complexes, the deprotonation of the ligands is important in realizing a larger structural stability of the equilibrium geometries. In the case of diketo-pyrphyrin planar ligand, with the singlet spin state, the better stability of the structure is given by an ionic contribution in the coordinative bond, formed between the positively charged metal ion and the negatively charged vertical ligand. The analysis performed with DLPNO-CCSD(T) showed that the fragment interaction in the triplet state is stronger than for the singlet state, due to the larger negative energy balance between the orbital deformation potential and the electrostatic/exchange energy contributions. The spin-orbit coupling is also influenced by

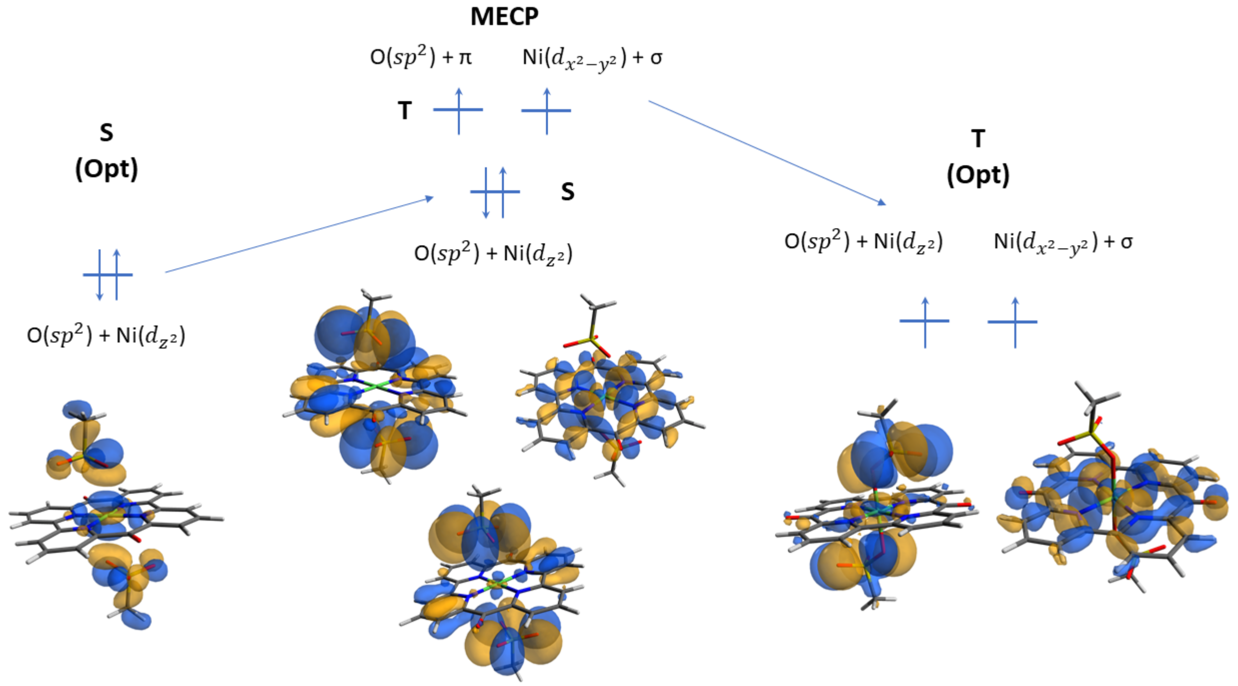
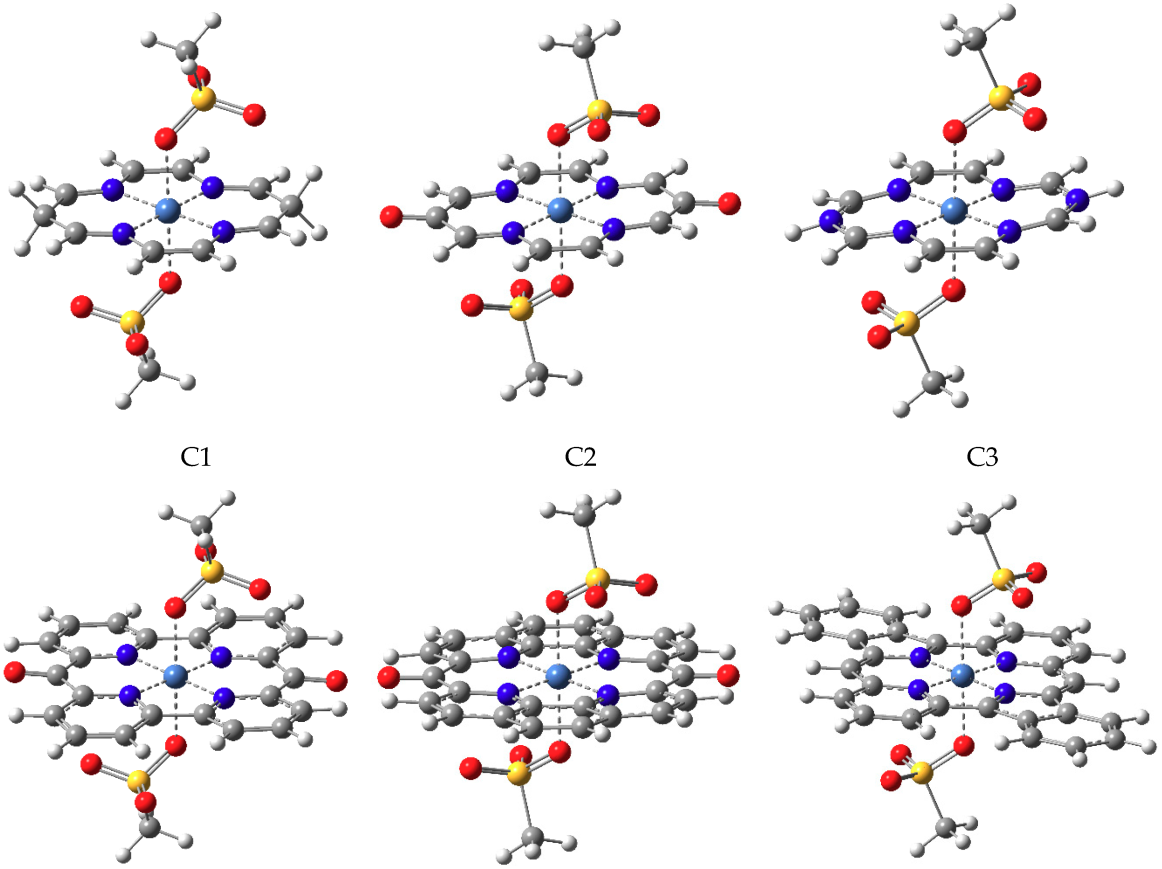


Figure 3.2. The orbitals transition scheme between the equilibrium geometries with singlet and triplet spin states for the DP+Mes metal-organic complex obtained at CAM-B3LYP-17-D3 level of theory.

the type of the planar and vertical ligands.

For the C1-C6 structures, the structural and energetic characterization was made for the singlet and triplet equilibrium structures together with the minimum energy crossing point (MECP). In Fig. 3.3, only the equilibrium geometries for the triplet configurations are presented.

Among this five configurations left, for the singlet spin state geometry, the C6 proves to have the most stable coordination, while for the triplet spin state geometry, the C1, C2, C4, and C5 cases show the lower energy minima. Despite the relative position of the minima, it is important to know the left and right barrier heights between the minima. The energy barrier between the MECP and the single state energy minima, for the C1 and C2, have a value lower than 0.1 eV, and for the C4 a value of 0.2 eV. In the case of C6, the lower barrier was obtained for the MECP - triplet state energy minima, with a value of 0.28 eV, which would be high enough to prevent the thermal transition phenomena to take place. The analysis over the LIESST phenomenon shows a more stable energetical configuration for the C4 and C6 cases than that for the C1, the C2, and the C5 complexes. Also, it can be noted that beside the energetical conditions, the singlet-triplet transition depends on the strength of the non-adiabatic and spin-orbit couplings[7–9].



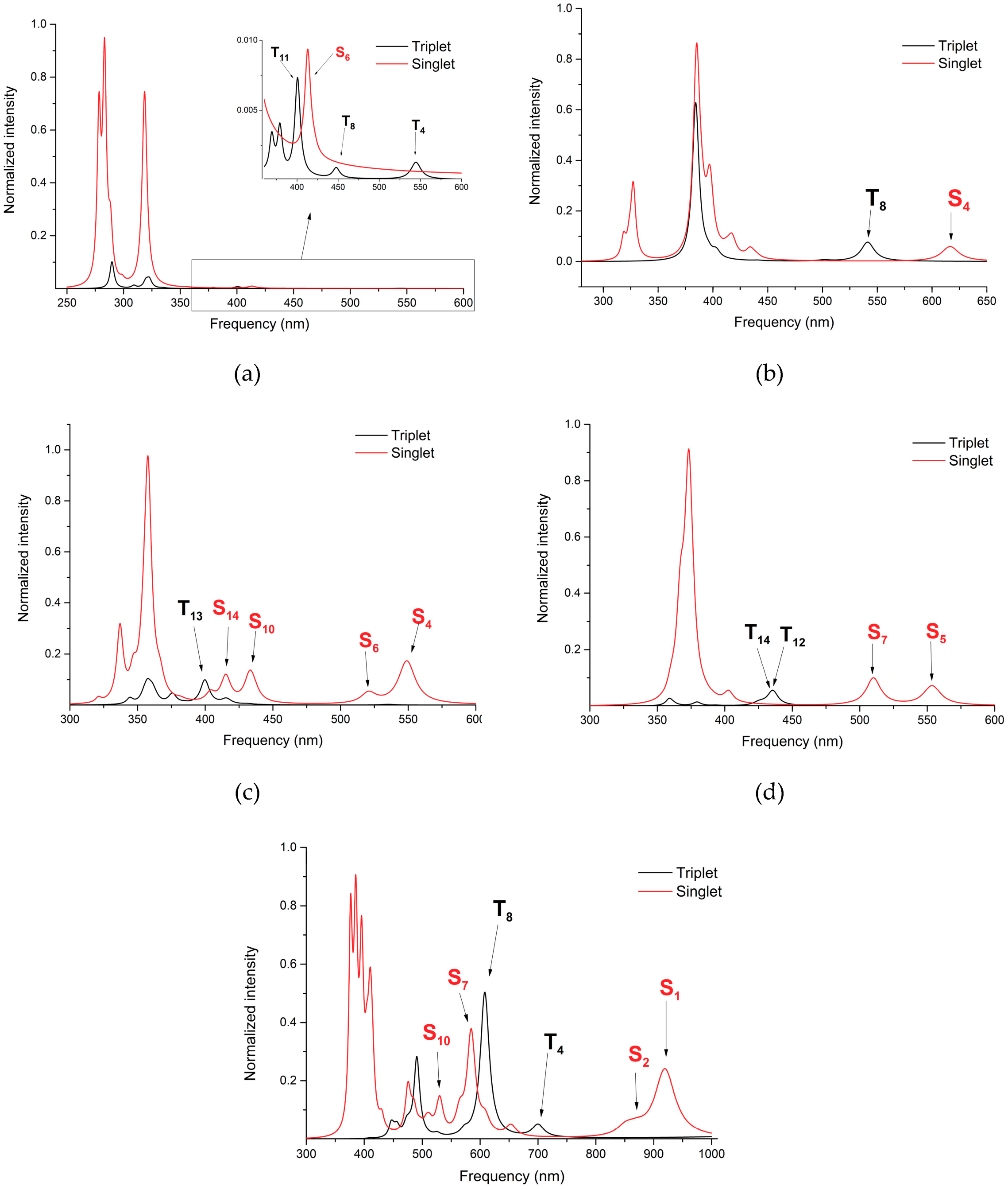
C1 C2 C3

C4 C5 C6

Figure 3.3. The equilibrium geometry configuration of the C1-C6 metal-organic structures with triplet spin configuration.

The first 30 electronic excited states and the UV spectra of absorption for the C1, C2, C4, C5, and C6 structures were computed using the M06/Def2-TZVP theory level. Figure 3.4 presents the spectral profiles for the C1, C2, C4,C5, and C6 complexes.

In the case of Ni(II)-based metal-organic complexes, different organic ligands were investigated in order to determine the structural reversibility, the geometrical stability, and the presence of an appropriate excitation frequency domain for these complexes. Depending on the ligand structure the octahedral coordinated metal-organic complexes could be energetically feasible for presenting spin-crossover properties. The aromatic fragments and the unsaturated bonds of the planar ligand have an important contribution in the photophysical and photochemical properties of the complex. The potential energy surface of the equilibrium geometries for the singlet and triplet spin states, together with the MECP of the spin states, are influenced by the types of the planar ligands. Each



(a) (b) (c) (d) (e)

Figure 3.4. The UV absorption spectra for of the (a) C1, (b) C2, (c) C4, (d) C5, and (e) C6 structures.

ligand presents a different UV spectral fingerprint, which can selectively determine the appropriate laser frequencies to initiate spin transitions. Another important aspect is the fact that the electronic charge distribution of the singlet and triplet states could induce spin transitions much easier. From all the complexes, the C_4 and C_5 proved to be the perfect candidates in order to be experimentally synthesized[10,11] and studied by spectroscopic techniques.

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4

Conclusions

The main aim of this thesis is to investigate two transfer processes at molecular level: the first class is represented by the electron transfer in donor-acceptor materials of interest for photovoltaic systems, and the second one is represented by the spin-transfer in supramolecular metal-organic systems with efficient spin-crossover properties of interest for optical, magnetic, and physical/chemical switches.

The first class of molecular systems studied as part of the present doctoral work belongs to photovoltaic materials, which are based on the formation and dynamics of electron–hole pairs induced by an external radiation. In order to understand the electron transfer processes occurring in donor-acceptor systems, we studied complexes composed of the star-shaped molecule Tris[4-(2-thienyl)phenyl]amine ($C_{30}H_{21}NS_3$), as donor, and the C_{70} fullerene, as acceptor. It was found that, the HOMO orbital of the donor-acceptor complex is quite similar to the HOMO of the $C_{30}H_{21}NS_3$ fragment, and the LUMO orbital is almost identical to the LUMO orbital of the C_{70} fragment. The time propagation of electron-hole pairs was achieved by applying the Cayley propagation scheme on the time-dependent Hamiltonian, consisting of the time-independent component defined by the molecular orbitals of the binary complex in the equilibrium geometrical configuration and the time-dependent component, which includes the light-matter interaction, by applying Gaussian shaped pulses. Löwdin population analysis defined on the basis of the time-dependent molecular orbital coefficients was used to trace the charge carrier dynamics in the donor-acceptor complex. The results show that electron transfer efficiency can be improved by modifying various characteristics of the electromagnetic field, such as intensity, frequency, pulse duration, etc. It was shown that using pulse frequencies in the resonance range of the donor-acceptor system, the electron transfer efficiency increases significantly. Electron transfer was also improved by increasing the pulse duration. At the same time, the importance of the relative position of the donor to the acceptor in terms of charge transfer efficiency was highlighted and the donor-acceptor configuration with the highest electron transfer was identified.

The second class studied in this thesis is represented by supramolecular systems, which exhibit spin-crossover behavior. The aim was to achieve the necessary conditions to obtain spin transitions induced by electromagnetic radiation such as, the efficient absorption of laser radiation, the existence of well-defined excited electronic states involved in the low spin-high spin transition, respectively the existence of the double-well potential characteristic for the two equilibrium states with different spins. As a first step, several search algorithms have been presented to locate the intersystem crossing points (the geometrical configuration at which the spin transition occurs). Then, the performance of several exchange-correlation (XC) DFT functionals was analyzed in order to describe as accurately as possible the spin transitions in the metal-organic complex of Ni-tetrakis(pentafluorophenyl)porphyrin (TPP), functionalized with a phenazopyridine (PAPy) arm, (NiTPP-PAPy). The results show that dispersion correction effects have a strong influence on the metal-nitrogen bond distances. In addition, the inclusion of a certain amount of Hartree Fock-exchange in the XC functional also has a large influence on the geometry of metal-organic complexes, since the large amount of HF-exchange alters the description of the multi-configuration character of the ligand bonds, while their absence maintains the self-interaction errors specific to the DFT exchange part. These errors can be significantly reduced by using a well-balanced combination of HF-exchange mixture with DFT-exchange.

In the next step, the performance of DFT and TD-DFT methods was tested with respect to the detailed description of the light-induced singlet-triplet spin transition in the case of two metal-organic complexes, namely, the previously mentioned NiTPP-PAPy and the Ni(II)-tetrakisporphyrin complexes functionalized with two phenazopyridine arms (NiTP-biPAPy) with square-pyramidal and octahedral coordination. In the first step the intersystem crossing point geometries were obtained using a penalty function algorithm which were subsequently validated by analyzing the energies of the singlet and triplet spin states along the direction of variation of the nitrogen atom between the two positions defined by the two equilibrium spin state geometries. The NiTPP-PAPy complex exhibits two intersystem crossing points, one of which is located on the minimum energy path of the singlet-triplet transition, along the ligand bond formed by the vertical nitrogen atom and the central nickel atom. It was found that the structural bistability and high barrier of the minimum-energy crossing point of the NiTPP-PAPy complex can prevent the spontaneous transitions induced by the thermal effects. In addition, theoretical calculations of vertical excitation energies reproduce experimental UV-Vis absorption spectra with good accuracy. Furthermore, the electronic excited states involved in the light-induced singlet-triple spin transition have been identified and their electronic nature has been characterized. At the same time the calculated spin-orbit coupling is also large enough so that the spin transition can be easily achieved. On the other hand, the asymmetric ISC geometry found for the NiTP-biPAPy complex with two phenazopyridine arms has a lower, but still sufficiently high, energy barrier than that of the symmetric ISC geometry configuration, hence it is more favorable to be involved in a spin transition.

Finally, the role of the structural configuration of the two macrocycles (porphyrin and diketopyrphyrin) considered as planar ligands in metal-organic complexes was investigated by characterizing the geometrical stability and structural reversibility due to spin transitions. In particular, the role of different planar ligands on the intensity of spin-orbit coupling along both the axial and vertical directions of the metal-ligand bond was investigated. An important correlation was observed between the atomic positions of ligand deprotonations, implicitly the direction of charge transfer between the metal ion and the ligand, and the spin transition properties in metal-organics with octahedral coordinations. The efficiency of spin transitions as a function of the spectral length of the laser excitation frequencies was also analyzed. It has been shown that excited electronic states with singlet or triplet spin configurations located in the upper part of the visible spectral range can be considered as electronic levels involved in an efficient and reversible process of spin transitions in the Ni(II)-diketopyrphyrin-bipyrrole complex both in terms of radiation absorption efficiency and the nature of the excited states which favors the change of spin states.

Investigations on photovoltaic and metal-organic materials are essential in predicting the controlled behavior of radiation-induced charge transfer processes in different donor-acceptor structures and spin-cross complexes. This work helps us to gain a better understanding of both photoinduced electron transfer dynamics in photovoltaic systems and the essential conditions required to build more efficient spin crossover systems.

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List of publications

Thesis related publications

1. **A.-A. Farcaş** and A. Bende: ”Theoretical modeling of the singlet–triplet spin transition in different Ni(II)-diketo-pyrphyrin-based metal–ligand octahedral complexes”, Physical Chemistry Chemical Physics, 23, 4784 (2021), (DOI).

   IF: 3.676
   AIS: 0.825

2. T. A. Beu, **A.-A. Farcaş** and A. Bende: ”Calculations of electron transfer in the tris[4-(2-thienyl)phenyl]amine–C70 donor-acceptor system.”, Chemical Physics Letters, 754, 137654 (2020), (DOI).

   IF: 2.328
   AIS: 0.373

3. **A.-A. Farcaş** and A. Bende: ”DFT study of adiabatic singlet-triplet energy gaps in Ni(II)-based macrocyclic-ligand supramolecular complexes.”, AIP Conference Proceedings, 2206, 030001 (2020), (DOI).

4. **A.-A. Farcaş** and A. Bende: ”Improving the Light-Induced Spin Transition Efficiency in Ni(II)-Based Macrocyclic-Ligand Complexes.”, Molecules, 24(23), 4249 (2019), (DOI).

IF: 3.267

AIS: 0.601

5. **A.-A. Farcaş**, T. A. Beu and A. Bende: ”Light-induced spin transitions in Ni(II)-based macrocyclic-ligand complexes: A DFT study.”, Journal of Photochemistry and Photobiology A: Chemistry, 376, 316–323 (2019), (DOI).

   IF: 3.306

   AIS: 0.453

Other publications

1. A. Bende, **A.-A. Farcaş** and V. Toşa: ”Theoretical study of light induced crosslinking reaction between pyrimidine DNA bases and aromatic amino acids.”, Frontiers in Bioengineering and Biotechnology, 9, 806415 (2022), (DOI).

   IF: 5.890

   AIS: 1.145

2. L. Máthé, C.P. Onyenegecha, **A.-A. Farcaş**, L.-M. Pioras-Timbolmaş, M. Solaimani, H. Hassanabadi, ”Linear and nonlinear optical properties in spherical quantum dots: Inversely quadratic Hellmann potential”, Physics Letters A, 397, 127262, (2021), (DOI).

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   AIS: 0.486

3. **A.-A. Farcaş**, A. Bende: ”Chapter Ten - The influence of monovalent and divalent metal cations on the stability of the DNA-protein interaction in the nucleosome core particle”, Advances in Quantum Chemistry, Volume 81, 269-290, (2020), (DOI).

   IF: 1.029

   AIS: 0.297

Conference contributions

1. A. Bende and **A.-A. Farcaş**, ”Structural stability of Ni (II)-based macrocyclic-ligand complexes with square-pyramidal and octahedral coordination configuration”, International Con-

ference on ”Processes in Isotopes and Molecules” (PIM), 25-27 September 2019, Cluj-Napoca, Romania, oral presentation.

2. **A.-A. Farcaş**, T. A. Beu and A. Bende, ”The influence of the metal-ligand charge transfer effects on the structural stability and the strength of the spin-orbit coupling in Ni(II)-based metal-ligand complexes”, 17th Central European Symposium on Theoretical Chemistry (CESTC), 9-12 September 2019, Burg Schlaining, Austria, poster presentation.
3. **A.-A. Farcaş**, T. A. Beu and A. Bende, ”Light induced singlet-triplet transition in Ni(II)-based macrocyclic-ligand complexes”, 18th International Conference on Density-Functional Theory and its Application (DFT), 22-26 July 2019, Alicante, Spain, poster presentation.
4. **A.-A. Farcaş**, T. A. Beu and A. Bende, ”The influence of the metal-ligand charge transfer effects on the structural stability and the strength of the spin-orbit coupling in Ni(II)-based metal-ligand complexes”, 10th Triennial Congress of the International Society for Theoretical Chemical Physics (ISTCP), 11-17 July 2019, Tromsø, Norway, poster presentation.
5. **A.-A. Farcaş** and A. Bende, ”Intersystem crossing in metalligand coordination complexes with pyramidal-planar and octahedral coordination configurations ”, 9th Conference on Molecular Modeling in Chemistry and Biochemistry (MOLMOD), 28-30 October 2018, Cluj Napoca, Romania, poster presentation.
6. **A.-A. Farcaş** and A. Bende, ”Modeling laser-induced spin crossover transitions using time-dependent density functional theory ”, 12th Joint Conference on Mathematics and Computer Science (MaCS), 14-17 June 2018, Cluj Napoca, Romania, oral presentation.
7. **A.-A. Farcaş** and A. Bende, ”Structural stability and laser induced singlet-triplet transition in Ni(II) macrocyclic ligand complex: A TD-DFT study ”, Central European Conference on Photochemistry (CECP), 4-8 February 2018, Bad Hofgastein, Austria, poster presentation.

Workshops

1. **A.-A. Farcaş**, ZCAM School on New Computational Methods for Attosecond Molecular Processes, 21-25 May 2018, Zaragoza, Spain.