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**PROMAZİN MOLEKÜLÜNÜN SEÇİLMİŞ
BİYOMOLEKÜLLERLE ETKİLEŞİMLERİNİN
FOTOFİZİKSEL VE HESAPSAL YÖNTEMLERLE
İNCELENMESİ**

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ÖNSÖZ

Fotofiziksel uyarılma ile gerçekleşen elektron transfer mekanizmaları ilk olarak çalışılmaya başlandığı 1950'lerden bu yana pekçok alanda dikkat çekmektedir. Fotosentez, biyolojik redoks mekanizmaları, yapay güneş enerjisi sistemleri gibi güncel ve son derece önemli alanlardaki çalışmalar da bu konuya olan ilgiyi arttırmaktadır.

Çalışmada incelenecek olan promazin mental bozukluklarda antipsikotik veya nöroleptik ilaç olarak, antikanser aktivitelerinde de yardımcı olarak yaygın olarak kullanılmaktadır. Bu nedenle fizyolojik şartlarda biyomoleküllerle etkileşimlerinin incelenmesi ve anlaşılması son derece önemlidir.

Çalışmada biyomolekül olarak tercih edilen dopamin, serotonin ve melatonin vücutta özellikle de beyinde duygusal durum, uyku, termal kararlılık ve biyolojik saat gibi temel işlevleri sinir sistemi yoluyla kontrol eden hormonlardır.

Moleküllerin özellikleri, etkileşimleri ve işlevleri yapılarına son derece bağlıdır. Bu nedenle etkileşim mekanizmalarının anlaşılabilmesi için öncelikle yapılarının (geometrilерinin) doğru olarak tanımlanması gerekir. Bu çalışmada incelenen tüm sistemlerin yapıları hesapsal yöntemler yardımıyla belirlenmiş; fotofiziksel özellikleri ise hem deneysel hem de hesapsal yöntemler kullanılarak belirlenmiştir.

Seçilen dört molekülün tek başlarına ve farklı moleküllerle komplekslerine ait çalışmalar bulunmasına rağmen birlikte incelendikleri ve komplekslerinin araştırıldığı bir çalışmaya rastlanmamıştır.

Bu çalışmanın amacı organik-biyokimyasal hibrit yük transfer sistemlerinin özelliklerinin promazinin dopamin, serotonin ve melatonin ile oluşturacağı donör-akseptör kompleksleri yardımıyla incelenmesidir. Bu sayede sağlık, elektronik, malzeme bilimi gibi birçok alanda kullanılabilecek yapay elektron transfer sistemlerinin geliştirilebilmesi için gerekli ön bilgileri elde edilecektir.

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ABBREVIATIONS

<u>Abbreviations</u>	<u>Definition</u>
PAHs	Polycyclic Aromatic Hydrocarbons
DFT	Density Functional Theory
CNTs	Carbon Nanotubes
SWCNTs	Single-Walled Carbon Nanotubes
MWCNTs	Multi-Walled Carbon Nanotubes
PZ	Promazine
DA	Dopamine
SE	Serotonin
MT	Melatonin
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
LE	Locally Excited
CT	Charge Transfer
DNA	Deoxyribo Nucleic Acid
OLED	Organic Light Emitting Diode

Promazin Molekülünün Seçilmiş Biyomoleküllerle Etkileşimlerinin Fotofiziksel ve Hesapsal Yöntemlerle İncelenmesi

ÖZET

Fenotiazin türevi olan promazin antipsikotik veya nöroleptik ilaç olarak kullanılmaktadır. Promazin yapısındaki π -elektron sistemleri nedeniyle floresans özelliğe sahiptirler, temel halde bulunan ve azot atomu içeren bir biyomolekülle, donör-akseptör elektron transfer kompleksleri oluşturabilirler. Bu çalışmada, promazinde bulunan gruplar elektron çekici grupları; donör olarak insan vücudunda doğal olarak bulunan ve üretilen azot atomu ve π -elektron sistemi içeren moleküller kullanılacaktır. Donör-akseptör kompleksleri arasında π - π etkileşimleri, dispersiyon kuvvetleri ve H-bağları oluşumu beklenmektedir.

Promazin ve hormonlar (dopamin, serotonin, melatonin) arasında oluşabilecek donör-akseptör sistemlerinin incelenmesi ve elektron transfer mekanizmalarının aydınlatılması, hem sağlık alanında ilaç tasarımında hem de modifiye nanomalzemelerin yapılmasında model olacaktır. Promazin ayrıca, floresans özelliğinden dolayı proteinlerin işaretlenmesinde biyosensör olarak da kullanılmaktadır. Bu amaçlarla seçilen bütün sistemlerin değişik polaritede hem deneysel hem de hesapsal incelemeleri yapılacaktır. Hesapsal olarak moleküller arasında oluşacak komplekslerin en kararlı geometrileri, dipol momentleri, Gibbs serbest enerji değerleri ve elektronik geçişleri belirlenecektir.

Anahtar Kelimeler: Elektron Transferi, DFT (Yoğunluk Fonksiyon Teorisi), İlaç, Hormonlar, UV, Floresans

Investigation of Interactions of Promazine with Selected Biomolecules by Photophysical and Computational Methods

ABSTRACT

Promazine, a phenothiazine derivative, is used as an antipsychotic or neuroleptic drug. Because of the presence of π -electronic system in its structure, promazine shows fluorescence properties. It may form donor-acceptor electron transfer complexes with a ground-state biomolecule which has a nitrogen atom. Promazine will be used as the acceptor in this study. Acceptor molecules will be chosen among molecules which are naturally occurring or synthesized in the human body with π -electronic system and nitrogen atoms. π - π interactions, dispersive forces and hydrogen bond formation are expected between donor-acceptor complexes.

Investigation of donor-acceptor complex formation between promazine and the hormones (dopamine, serotonin, melatonin) and determination of electron transfer mechanisms are important and will be a model for drug design studies and production of modified nanomaterials. Promazine is also used as a biosensor for marking proteins due to its fluorescence properties. All the systems will be investigated in different polarities using experimental and computational techniques. Most stable complexes will be determined computationally and their geometries, dipole moments, Gibbs free energies and their electronic transitions will be determined.

Keywords: Electron Transfer, DFT (Density Functional Theory), Drug, Hormones, UV, Fluorescence

1. INTRODUCTION

All photochemical and photophysical processes are initiated by the absorption of a photon of visible or ultraviolet radiation leading to the formation of an electronically-excited state. Photophysically excited electron transfer processes play an important role in many scientific fields. A photophysically excited molecule is a better donor or acceptor compared to its ground-state form. This molecule causes chemical changes in neighboring ground-state molecule by electron transfer mechanism, thus making it photophysically sensitive. Charge transfer complexes and energy transfer processes formed by this mechanism play also important roles in biochemical processes.

Complex formation in the excited state by charge transfer which is one of the most important fields of excited state chemistry has been first studied by Förster and Kasper [1], Leonhardt and Weller [2], and Mataga et al. [3]. Their studies have been followed by the others as applications in photobiology, solar energy conversion, sensors and molecular electronic devices [4, 5, 6].

First studies related to electron transfer started about sixty years ago [7, 8]. Understanding the electron transfer mechanism will enable many fundamental and practical applications including photosynthesis, biological redox mechanisms and design of solar battery devices. Additionally, combination of experimental and theoretical data will provide useful information on producing molecular devices and designing new drugs.

Biologically important molecules like porphyrins, basic nucleotides, aromatic amino acids, some drugs are aromatic and they have π -electron systems. The biochemical behavior of these molecules is affected by their photophysical properties which arise from the electronic excitation of these molecules by internal and external processes. Dopamine and serotonin act in the body as hormones and they are also neurotransmitters responsible for regulation of many fundamental processes in the brain like emotional state and control, sleep, awakesness, food intake and thermal stability [9]. On the other hand, melatonin, another hormone, regulates the biological clock. Its most important function is to control many physiological and behavioral processes triggered by environmental light-darkness cycle [10]. Promazine is a psychotropic drug which is used widely in mental disorders [11-13] and anticancer activities [14-21]. Its interactions in metabolism

with the chosen molecules (dopamine, serotonin and melatonin) are important in terms of its biological activity.

Since these molecules are biologically important, they were studied by different groups, mostly because of their pharmaceutical importance [22-29]. Some studies also included some structural and chemical properties [23-25]. Most recently these molecules began to attract attention for use in production of biocompatible materials [24]. These studies focused on single molecules and there are no reported studies on their intra or inter molecular complexes either in ground state or in excited state.

There are studies on intramolecular complex formation of promazine with some biomolecules in the literature; but, there are no reported studies on its intermolecular interactions. Stability of intermolecular complexes depends on total interaction energy (exchange, electrostatic and dispersive forces) because of π electrons (in some cases n electrons) between molecules.

The aim of this study is to understand charge transfer by light excitation of a photoactive components and modify the electronic interactions such as van der Waals forces and hydrogen bonding mechanisms as well as the factors affecting these processes between promazine and biologically important molecules dopamine, serotonin and melatonin.

In this study, intermolecular interactions between photophysically excited promazine and naturally occurring hormones (dopamine, serotonin, melatonin) in the human body at ground-state will be investigated using experimental and computational tools. Excitation of chromophoric systems and subsequent photochemical processes are still difficult to predict and to treat theoretically, even in some liquid phase. Therefore, the outcome of the work is important as it is expected to gain detailed insight about donor-acceptor systems composed of organic-biological hybrid components. This information will provide useful information for many related fields including health, electronics, materials science etc.

2. THEORY

2.1. The Interaction of Light with Matter

The interaction of light and matter as a natural phenomenon and/or as an artificial process enters most branches of science, from medicine to material science [30, 31]. Our life depends on photosynthesis, a photochemical process taking place in nature. We are encircled by substances that are produced by natural or artificial photochemical reactions. Many of most common functions exploited in our technological environment, from signal processing, storage and display to the use of pigments, sensors and sensitizers are based on the interaction of light with matter. Solar energy is artificially converted into useful energy forms by photochemical and photophysical processes [32, 33]

Sometimes electronic excitation can result in chemical changes, such as the fading of dyes, photosynthesis in plants, suntans, or even degradation of molecules. On other occasions, the electronically-excited state may undergo deactivation by a number of physical processes, either resulting in emission of light (luminescence) or conversion of the excess energy into heat, whereby the original ground state is reformed. Electronically-excited states can also interact with ground-state molecules, resulting in energy-transfer or electron-transfer reactions provided certain criteria are met.

The atoms in the material body have only two energy levels as a ground state M and an excited state M^* . Excited states are formed by the absorption of radiation by ground states;



and excited states can then decay back to the ground state through stimulated emission;



The concentrations of ground and excited states of M be $[M]$ and $[M^*]$ respectively and isotropic photon density of the radiation be I , then the kinetic equations are;

$$\text{Absorption} \quad \quad \quad d[M^*] / dt = BI[M] \quad \quad \quad (2.3)$$

$$\text{Spontaneous emission} \quad \quad d[M^*] / dt = A[M^*] \quad \quad \quad (2.4)$$

$$\text{Stimulated emission} \quad \quad d[M^*] / dt = -BI[M^*] \quad \quad \quad (2.5)$$

In these equations A and B are known as Einstein coefficients. These constants give the transition probabilities.

2.1.1 The Transition Moments

The Einstein coefficients are related to the quantity which describes the transition probability, known as the transition moment. During an electron transition, an electron jumps from one orbital to another. Its distance from the nucleus changes, so there is a change in the instantaneous dipole moment. The greater this change, the more probable the transition because it is the interaction between this transition dipole and the electric vector of light.

In an atom of spherical symmetry or a molecule which has an inversion centre there is no permanent dipole moment. They can have large transition moments, as these describe in effect the motion of an electron from one orbital to another. The overall symmetry is restored after electron jump.

2.1.2 The Energy of Light

In order of increasing energy, molecules have translational, rotational, vibrational and electronic excited states. The electronic excited states only lead to photochemistry, since their energies correspond to the frequencies of near IR, visible and near UV light. An electronic transition brings an atom or molecule from the ground state to one of its excited states, or vice versa.

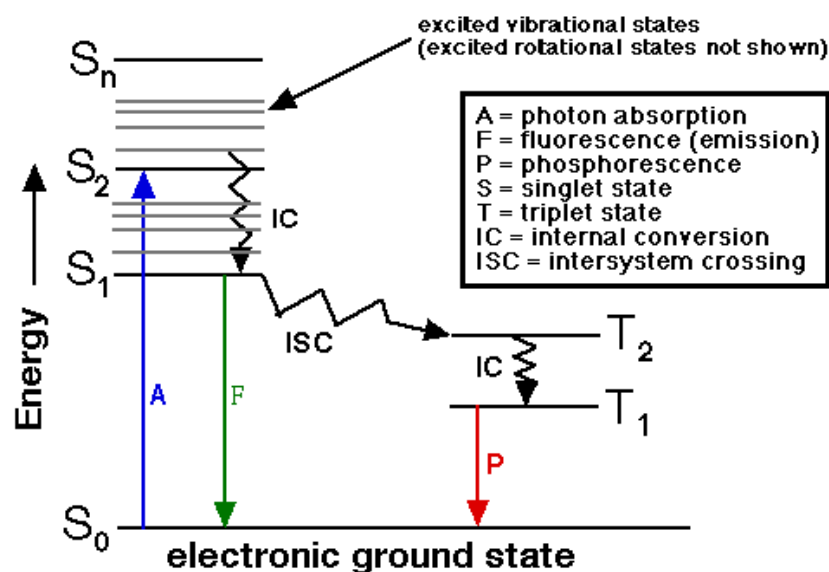


Figure 2.1. Jablonski diagram

The absorption and emission of light is nicely illustrated by the energy-level diagram suggested by A. Jablonski [34]. A typical Jablonski diagram is shown in figure 2.1. The singlet ground, first, and second electronic states are depicted by S_0 , S_1 , and S_2 , respectively. At each of these electronic energy levels the fluorophores can exist in a number of vibrational energy levels. In this diagram, solvent effects are excluded. The transitions between states are shown as vertical lines to illustrate the instantaneous nature of light absorption. Transitions occur in about 10^{-15} s, a time too short for significant displacement of nuclei. This is the Franck-Condon principle [35].

Following light absorption, several processes usually occur. A fluorophore is usually excited to some higher vibrational level of either S_1 or S_2 . With a few rare exceptions, molecules in condensed phases rapidly relax to the lowest vibrational level of S_1 . This process is called internal conversion and generally occurs in 10^{-12} s or less. Since fluorescence lifetimes are typically near 10^{-8} s, internal conversion is generally complete prior to emission. Hence, fluorescence emission generally results from a thermally equilibrated excited state, that is, the lowest-energy vibrational state of S_1 . Return to the ground state typically occurs to a higher excited vibrational ground state level, which then quickly (10^{-12} s) reaches thermal equilibrium.

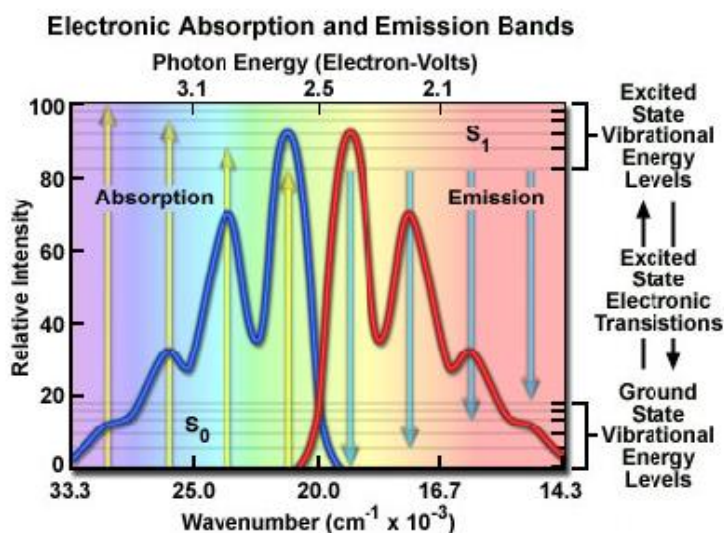


Figure 2.2. Electronic absorption and emission bands

The emission to higher vibrational ground states is that the emission spectrum is typically a mirror image of the absorption spectrum of the $S_0 \rightarrow S_1$ transition. This similarity occurs because electronic excitation does not greatly alter the nuclear geometry. Hence, the spacing of the vibrational energy levels of the excited states is similar to that of the ground state. As a result, the vibrational structures seen in the absorption and the emission spectra are similar (figure 2.2).

Molecules in the S_1 state can also undergo a spin conversion to the first triplet state, T_1 . Emission from T_1 is termed phosphorescence and is generally shifted to longer wavelengths (lower energy) relative to the fluorescence. Conversion of S_1 to T_1 is called intersystem crossing. Transition from T_1 to the singlet ground state is forbidden, and, as a result, rate constants for triplet emission are several orders of magnitude smaller than those for fluorescence.

Another general property of fluorescence is that the same fluorescence emission spectrum is generally observed irrespective of the excitation wavelength. This is known as Kasha's rule, although Vavilov reported in 1926 that quantum yields were generally independent of excitation wavelength. Upon excitation into higher electronic and vibrational levels, the excess energy is quickly dissipated, leaving the fluorophore in the

lowest vibrational level of S_1 . This relaxation occurs in about 10^{-12} s. Because of this rapid relaxation, emission spectra are usually independent of the excitation wavelength.

Most studies of the fluorescence and absorption spectra and other photo physical properties of aromatic molecules are made in solution. The emitting or absorbing molecule is thus exposed to the influence of the surrounding molecules of the solvent, which can produce significant changes in its photophysical properties. The observed spectral and photophysical parameters are characteristic of the molecule in its solvent environment rather than of the isolated molecule.

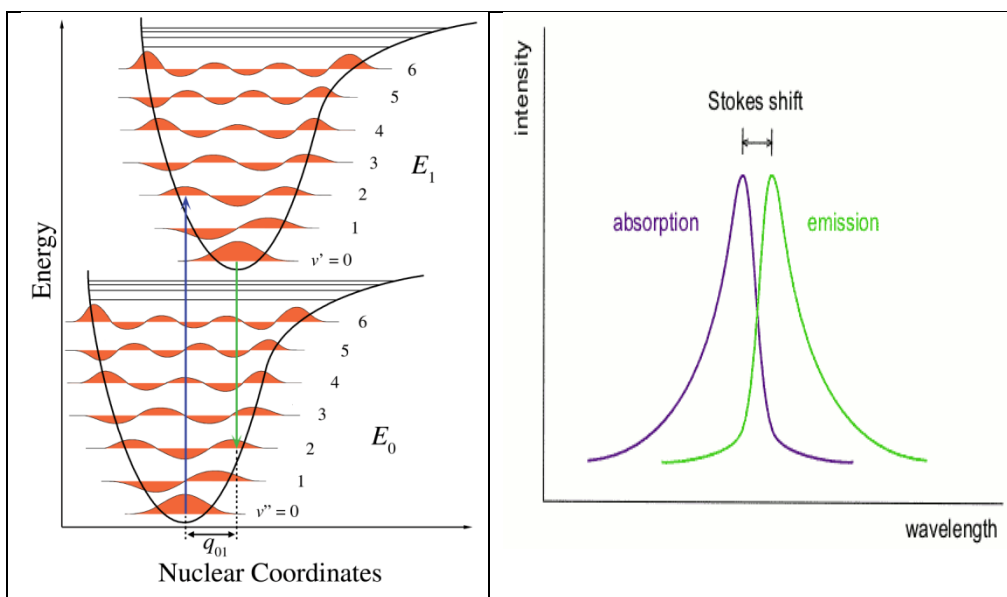


Figure 2.3. Potential energy

In solution each of the spectral parameters is normally shifted to lower energies, and the 0-0 transitions no longer coincide (figure 2.3), so that $\Delta\nu_A - \Delta\nu_F > 0$, where ν_A and ν_F represent the transitions energies of absorption and fluorescence, respectively. There are two types of intermolecular interaction responsible for the spectral changes in a solvent medium, which are arbitrarily divided into general and specific solvent effects. By a general solvent effect (universal interaction) those which results from the dielectric constant (ϵ) refractive index (n) are meant. These

physical constants reflect the freedom of the motion of the electrons in the solvent molecules, and the dipole moments of the molecules. The spectral changes due to universal interaction are described in terms of the Onsager theory of dielectrics [36] and the Franck-Condon principle [37]. Specific solvent effects refer to specific chemical interactions between the fluorophore and the solvent molecules, such as the formation of hydrogen bonds, complexes or exciplexes. Both general and specific solvent interactions can result in significant spectral shifts. General solvent effects are always expected to be present. In contrast, specific solvent effects will depend upon the precise chemical structures of the solvent and solute.

Polarity sensitive spectral changes of polyaromatic hydrocarbons results from interactions of the dipole moment of the excited fluorophore with reactive fields induced in the surrounding solvents, and from hydrogen bonding between the fluorophore and solvent molecules. The dipole moments of the electronically excited compounds are larger than those of the corresponding ground state species. This situation perturbs the solute-solvent structure and the lifetime of the first excited state changes depending on the solvent polarity [36].

In non-polar solvents the quenching of the fluorescence of aromatic electron donors (D) by electron acceptors (A) is usually associated with the formation of an intermediate exciplex $^1(A\cdots D^+)^*$, characterized by a new fluorescent band. The application of nanosecond laser photolysis methods has subsequently fielded the absorption of spectra of several exciplex [38]. In polar solvents such as methanol or acetonitrile, the exciplex emission is extremely weak and the corresponding absorption is replaced by that of the relatively long lived ionic dissociation products A^- and D^+ . The systems formed by the increasing solvent polarity effects were investigated by some researchers [39-41].

2.2 Excited States of Molecules

2.2.1 Diatomic Molecules

In a very simple molecule such as hydrogen, H_2 , two H atoms come together to form a chemical bond. The two atomic orbitals interact when

they are very close together. And this interaction can lead to two opposite situations, as shown in figure 2.4

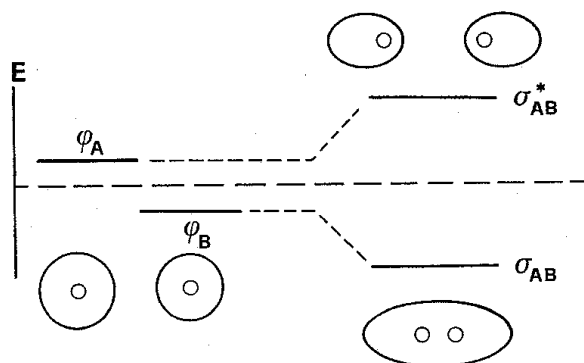


Figure 2.4. The interaction of two atomic orbitals leads to the formation of bonding and antibonding molecular orbitals of different energies.

A bonding molecular orbital is formed if two electrons are found in the space between the nuclei; they provide a shield between the two positively charged protons so that their electrostatic repulsion is lowered. An antibonding molecular orbital is formed if the two electrons are localized outside the internuclear region, so that the repulsion of the nuclei is actually greater than in the case of two separate atoms at the same distance. The energies of the bonding and antibonding orbitals are therefore lower and higher, respectively, than that of the constituent atomic orbitals.

Two orbitals play a special role and are known as “Highest Occupied Molecular Orbital (HOMO)” and the “Lowest Unoccupied Molecular Orbital (LUMO)”, these labels are referring of course to the situation in the ground state. The transition of an electron between these orbitals corresponds to the lowest excited state(s), e.g. triplet T_1 and singlet S_1 .

2.2.2. Cyclic Conjugated Systems: Aromatic Molecules

The molecule of benzene is the simplest representative of a very large family of cyclic conjugated molecules. Aromatic molecules are formed essentially through the substitution, linking and fusion of the benzene ring which consists of six carbon atoms linked in a hexagonal cycle. Since there

are six p orbitals which interact to form the molecular orbitals, there will be three bonding π orbitals and three antibonding π^* orbitals.

2.2.3. Types of Transitions

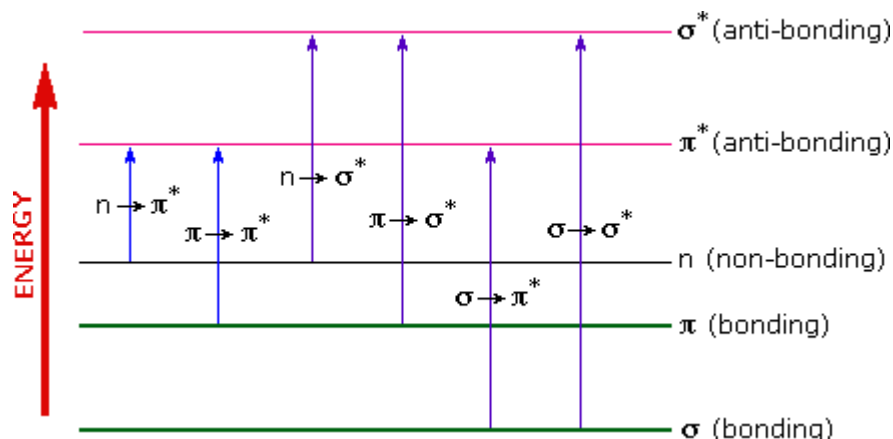


Figure 2.5. Energy diagram of transitions

There are some typical transitions as shown in the figure 2.5.

$\sigma \rightarrow \sigma^*$ transitions

An electron in a bonding σ orbital is excited to the corresponding antibonding orbital. The energy required is large. For example, methane (which has only C-H bonds, and can only undergo $\sigma \rightarrow \sigma^*$ transitions) shows an absorbance maximum at 125 nm. Absorption maxima due to $\sigma \rightarrow \sigma^*$ transitions are not seen in typical UV-Vis. spectra (200 - 700 nm).

$n \rightarrow \sigma^*$ transitions

Saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of $n \rightarrow \sigma^*$ transitions. These transitions usually need less energy than $\sigma \rightarrow \sigma^*$ transitions. They can be initiated by light whose wavelength is in the range 150 - 250 nm. The number of organic functional groups with $n \rightarrow \sigma^*$ peaks in the UV region is small.

n- π^* and π - π^* transitions

Most absorption spectroscopy of organic compounds is based on transitions of n or π electrons to the π^* excited state. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200 - 700 nm). These transitions need an unsaturated group in the molecule to provide the p electrons.

n $\rightarrow\pi^*$ absorption is characteristic of molecules possessing chromophores with multiply bonded hetero-atoms (e.g. C=O, C=N, C=S, N=N, N=O). It is of low intensity ($f \approx 10^{-2} - 10^{-4}$) being symmetry or overlap forbidden, it is normally the band occurring at the wavelength. Molar absorptivities from n- π^* transitions are relatively low, and range from 10 to 100 L mol⁻¹ cm⁻¹. π - π^* transitions normally give molar absorptivities between 1000 and 10,000 L mol⁻¹ cm⁻¹.

The solvent in which the absorbing species is dissolved also has an effect on the spectrum of the species. Peaks resulting from n- π^* transitions are shifted to shorter wavelengths (blue shift) with increasing solvent polarity. This arises from increased solvation of the lone pair, which lowers the energy of the n orbital. Often (but not always), the reverse (i.e. red shift) is seen for π - π^* transitions. This is caused by attractive polarisation forces between the solvent and the absorber, which lower the energy levels of both the excited and unexcited states. This effect is greater for the excited state, and so the energy difference between the excited and unexcited states is slightly reduced - resulting in a small red shift. This effect also influences n- π^* transitions but is overshadowed by the blue shift resulting from solvation of lone pairs.

Charge-transfer (CT) transitions

Many inorganic species show charge-transfer absorption and are called charge-transfer complexes. For a complex to demonstrate charge-transfer behaviour, one of its components must have electron donating properties and another component must be able to accept electrons. Absorption of radiation then involves the transfer of an electron from the donor to an orbital associated with the acceptor.

Molar absorptivities from charge-transfer absorption are large (greater than 10,000 L mol⁻¹ cm⁻¹). Mixtures of electron donors and electron acceptors in solution often exhibit a new absorption band. This new band is not carry properties of components alone. It is attributed to the presence in such mixtures of a donor acceptor complex (DAC). The transition is referred to as a charge transfer (CT) transition and general is broad and structureless. The nature of the bonding in DACs and the theory of CT absorption have been worked out by Mulliken. The ground state of A DAC is described by a wavefunction:

$$\psi_{(S_0)} = a\psi_{(DA)} + b\psi_{(D^+A^-)} \quad (2.6)$$

In which $\psi_{(DA)}$ corresponds to a `no-bond` structure, the components being held only by weak intermolecular forces such as hydrogen bonding and dipole-dipole interaction and $\psi_{(D^+A^-)}$ corresponds to the structure in which an electron has been totally transferred from the donor to the acceptor. The wavefunction for the excited states of the DAC is then given by;

$$\psi_{(S_1)} = a\psi_{(D^+A^-)} - b\psi_{(DA)} \quad (2.7)$$

In generally, $b \ll a$, so that $\psi_{(S_0)} \sim \psi_{(DA)}$ and $\psi_{(S_1)} \sim \psi_{(D^+A^-)}$. Thus, the spectroscopic transition corresponds approximately to the light induced transfer of an electron from the donor to the acceptor, and the named charge-transfer transition. And there is very little charge-transfer in the ground state.

The energetics of DACs can be explored with energy diagrams. In figure 2.6, ΔH_0 and ΔH_1 are the energies of formation of the ground state of DAC from D and A, and the excited state from D⁺ and A⁻, and A_A and I_D are the electron affinity of the acceptor and the ionization potential of the donor. The energy of the CT transition (ΔE_{CT}) is written by;

$$\Delta E_{CT} = I_D - A_A - (\Delta H_1 - \Delta H_0) \quad (2.8)$$

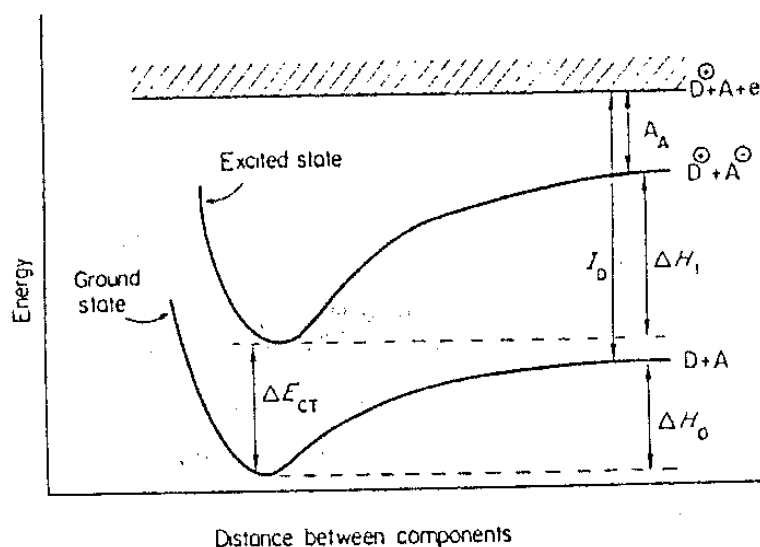


Figure 2.6. Energetics of donor-acceptor complexes.

2.3. The Reactions of the Electronically Excited Molecules

For the reaction to be observable by fluorescence measurements, the reaction time must be comparable to or shorter than the mean lifetime of the excited molecules. The reactions of the electronically excited molecule can be classified as follows [42].

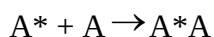
2.3.1 Quenching of fluorescence (probably electron transfer)

An excited molecule, A^* , loses its energy through interaction with molecule B instead of fluorescence radiation.



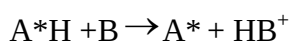
2.3.2 Complex formation

An excited form of molecule, A^* , can undergo complex formation either with the same molecule in ground state, A, or with another molecule, in ground state, B



2.3.3 Acid base reactions

The acid-base reactions can proceed as follows;



2.4. Solvent Effects on Emission Spectra

Emission from fluorophores generally occurs at longer wavelengths than those at which absorption occurs. This loss of energy is due to dynamic processes which occur following light absorption (figure 2.7).

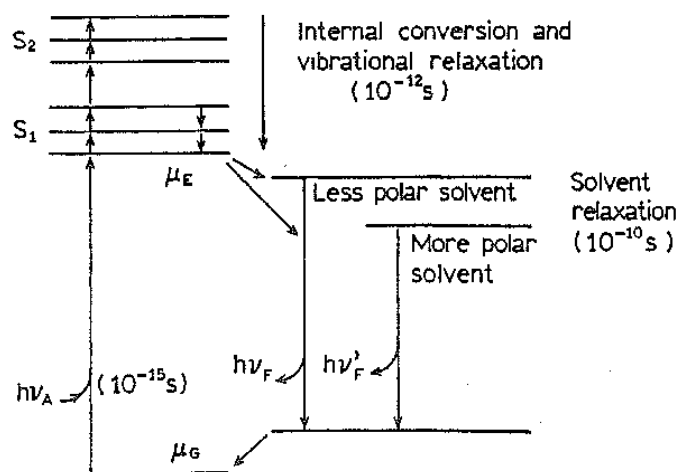


Figure 2.7. Jablonski diagram for fluorescence with solvent relaxation.

On the other hand, fluorescence lifetimes are usually longer than the time for solvent relaxation so that the emission spectra are pattern of the solvent relaxation. But absorption of light occurs in about 10⁻¹⁵ s. This time is too short for motion of the fluorophore or solvent and this can explain

why the absorption spectra are less sensitive to solvent polarity than emission spectra.

2.5. Electron and Energy Transfer

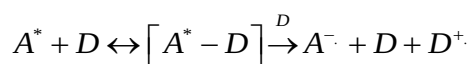
When the concentration of a solute is increased, it is commonly observed that a decrease in the intensity of its fluorescence. This is called concentration quenching. It has been found that such quenching is accompanied by the appearance of a new emission at longer wavelengths. And the intensity of this band is increased with concentration. For example, the violet fluorescence of pyrene in dilute solution is replaced by a blue fluorescence with increasing pyrene concentration. Förster and Kasper showed that these phenomena could be explained by the formation and fluorescence of a pyrene excimer [43].

Many aromatic hydrocarbons and derivatives exhibit a second type of fluorescence in concentrated solution, known as excimer fluorescence [1]. Benzene, naphthalene and their methyl derivatives are the other examples of excimer systems.

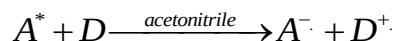
If two molecules form a complex in the excited state it is called as exciplex (excited complex). These types of complexes form because of the diffusional quenching of two molecules and called encounter complexes. As a result, the charge distribution shifts from the donor molecule to the acceptor and this is called the intermolecular electron transfer.

Exciplexes with a close charge separation can be explained as positive charge on donor and negative charge on acceptor are localized ($\beta > \alpha$). Charge separation has been seen by the nonradiative transition or emission (exciplex fluorescence) in nonpolar solvents. It can be usually separated in solvated radical ion forms in more polar solvents.

Exciplexes may be deactivated by another ground-state molecule, and it has been suggested that electron transfer may play a role in this deactivation (where A^* is an excited acceptor and D is a donor).



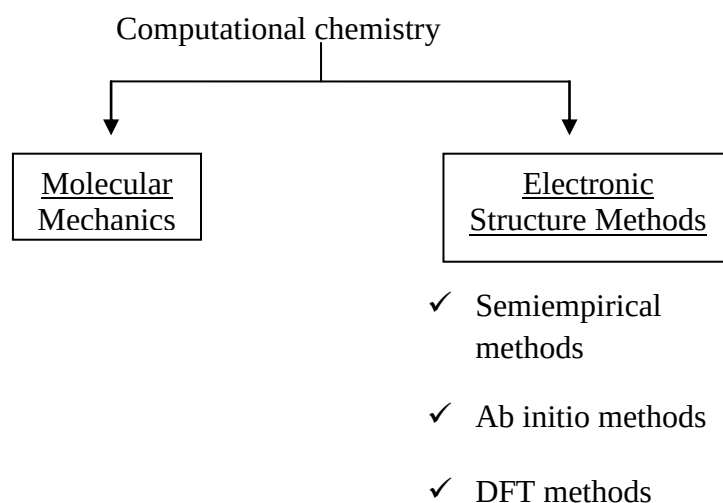
A photoexcited molecule may react with a ground-state molecule to undergo electron transfer at an encounter distance yielding a radical ion pair in polar media. These radical ions tend to undergo rapid back.



In order to convert light energy into chemical energy in an efficient manner, the rate of back electron transfer must be controlled or retarded.

2.6. Computational Theory

Chemistry has been known as an experimental science and until recently no molecule could be investigated till it was synthesized or found in nature. Computational chemistry has allowed scientists to predict the structures, energies, and other properties of molecules by chemical calculations. The major difference between the experimental and computational techniques is that calculations can be performed easily for compounds that have never been synthesized, or even do not exist under normal conditions. One can calculate molecular structure, heat of formation, dipole moment, ionization potentials, charge densities, etc. in a single process whereas this is impossible in one experiment.



The computational methods are classified in two main groups: force field or molecular mechanics calculations and electronic structure methods.

Electronic structure methods also consist of semiempirical methods, ab initio and DFT methods.

2.6.1 Molecular Mechanics Methods

Molecular mechanics simulations use the laws of classical physics to predict the structures and properties of molecules. There are many different molecular mechanics methods. And each one is characterized by its particular force field. Molecular mechanics calculations do not explicitly treat the electrons in a molecular system. This method achieves calculations depending on the interactions among the nuclei. Electronic effects are implicitly included in force fields through parametrization. This approximation makes molecular mechanics computations very short time and it is useful for very large systems.

2.6.2 Electronic Structure Methods

Electronic structure methods use the laws of quantum mechanics for their computations. Wavefunctions are used to describe the state of a system in quantum mechanics and they are denoted by ψ . The wavefunction depends only on the spatial coordinates of the system and time. The properties of a system are usually time independent or time averaged. For a complete description of an atom, the Schrödinger Equation which includes the relations of the electrons with the nucleus among themselves is used

$$H \psi = E \psi \quad (2.12)$$

H = Hamiltonian operator of the Schrödinger Equation

ψ = wavefunction

E = total energy of the system

The Hamiltonian operator is used to calculate energies (eigenvalues) and the wave function which is an eigenfunction of the operator H .

For any but the smallest systems, however, exact solutions to the Schrödinger equation are not computationally practical. Electronic structure

methods are characterized by their various mathematical approximations to its solution. Born–Oppenheimer is one of the approximations where the coupling between the nuclei and electronic motion is neglected. Electrons move faster with respect to the nuclei which have larger mass; so, nuclei can see an averaged potential of electrons whereas electrons can see any positional change in nuclei. It can be separated into nuclear and electronic wavefunction as in the equation.

$$H = T_n + T_e + V \quad (2.13)$$

$$\Psi = \Psi_n + \Psi_e \quad (2.14)$$

Hamiltonian is shown in Eq.(2.13). T_n denotes the kinetic energy of the nuclei, T_e stands for the kinetic energy of the electrons and V represents the potential energy. The nuclei move slower than the electrons, the kinetic energy of the nuclei can be neglected and the repulsion between the nuclei can be considered to be constant during the optimization (Born–Oppenheimer approximation) [44].

Another significant simplification can be obtained by introducing independent-particle models, where the motion of one electron is considered to be independent of the dynamics of all other electrons. This model means that the interactions between the particles is approximated, either by neglecting all but the most important one, or by taking all interactions into account in an average fashion. Within electronic structure theory, only the latter has an acceptable accuracy, and is called Hartree–Fock (HF) theory. In the HF model, each electron is described by an orbital, and the total wave function is given as a product of orbitals.

2.6.2.1 Semiempirical Methods

Semi-empirical methods are characterized by their use of parameter derived from experimental data in order to simplify the approximation to the Schrödinger Equation. As such, they are relatively inexpensive and can be practically applied to very large molecules. AM1 and PM3 are commonly employed methods.

2.6.2.2 Ab initio Methods

Ab initio methods try to solve the Schrödinger equation without fitting parameters to experimental data. Actually, *ab initio* methods also make use of experimental data, but in a somewhat more subtle fashion. Many different approximate methods exist for solving the Schrödinger equation, and which one to use for a specific problem is usually chosen by comparing the performance against known experimental data. Experimental data thus guides the *selection* of the computational model, rather than directly *entering* into the computational procedure.

One of the approximations inherent in essentially all *ab initio* methods is the introduction of a basis set. Expanding an unknown function, such as a molecular orbital, in a set of known functions is not an approximation if the basis set is *complete*. However, a complete basis set means that an infinite number of functions must be used, which is impossible in actual calculations. When a finite basis set is used, only the components of the MO along those coordinate axes corresponding to the selected basis functions can be represented. The smaller the basis set, the poorer is the representation. The *type* of basis functions used also influence the accuracy.

There are two types of basis functions commonly used in electronic structure calculations: *Slater Type Orbitals* (STO) and *Gaussian Type Orbitals* (GTO).

Slater type orbitals have the functional form shown in Eq (2.15).

$$\chi_{\zeta,n,l,m}(r,\theta,\phi) \propto Y_{l,m}(\theta,\phi) r^{n-1} e^{-\zeta r} \quad (2.15)$$

Here N is a normalization constant and $Y_{l,m}$ are spherical harmonic functions. The exponential dependence on the distance between the nucleus and electron mirrors the exact orbitals for the hydrogen atom. STO describes fairly well the radial electron distribution. However, STO is difficult to handle because integrations can not be calculated analytically.

Gaussian type orbitals can be written in terms of polar or Cartesian coordinates as shown in eq (2.16)

$$\chi_{\zeta,n,l,m}(r,\theta,\phi) \propto Y_{l,m}(\theta,\phi) r^{2n-2-l} e^{-\zeta r^2} \quad (2.16)$$

GTO describes less satisfactorily the radial electron distribution. However, GTO is easy to handle because integrations can be calculated analytically.

2.6.2.3 Density Functional Methods

The basis for Density Functional Theory (DFT) is the proof by Hohenberg and Kohn [45] that the ground state electronic energy is determined completely by the electron density ρ .

The significance of the Hohenberg–Kohn theorem is perhaps best illustrated by comparing it with the wave function approach. A wave function for an N electron system contains $4N$ variables, three spatial and one spin coordinate for each electron. The electron density is the square of the wave function, integrated over $N - 1$ electron coordinates, and each spin density only depends on three spatial coordinates, independent of the number of electrons. While the complexity of a wave function increases exponentially with the number of electrons, the electron density has the same number of variables, independent of the system size. The goal of DFT methods is to design functionals connecting the electron density with the energy. A wave function and the electron density are thus functions, while the energy depending on a wave function or an electron density is a functional. We will denote a function depending on a set of variables with parenthesis, $f(\mathbf{x})$, while a functional depending on a function is denoted with brackets, $F[f]$.

Early attempts at designing DFT models (actually predating wave mechanics) tried to express all the energy components as a functional of the electron density but these methods had poor performance, and wave function-based methods were consequently preferred. The success of modern DFT methods is based on the suggestion by Kohn and Sham in 1965 that the electron kinetic energy should be calculated from an auxiliary set of orbitals used for representing the electron density. The exchange–correlation energy, which is a rather small fraction of the total energy, is then the only unknown functional, and even relatively crude approximations

for this term provide quite accurate computational models. The simplest model is the local density approximation, where the electron density is assumed to be slowly varying, such that the exchange–correlation energy can be calculated using formulas derived for a uniform electron density. A significant improvement in the accuracy can be obtained by making the exchange–correlation functional dependent also on the first derivative of the density, and further refinements also add the second derivative and mix Hartree–Fock exchange into the functional. Density functional theory is conceptually and computationally very similar to Hartree–Fock theory, but provides much better results and has consequently become a very popular method. The main problem in DFT is the inability to systematically improve the results, and the known failure to describe certain important features, such as van der Waals interactions.

3. MATERIAL AND METHODS

3.1 Materials

Molecular structures of the studied molecules are shown in Figure 3.1.

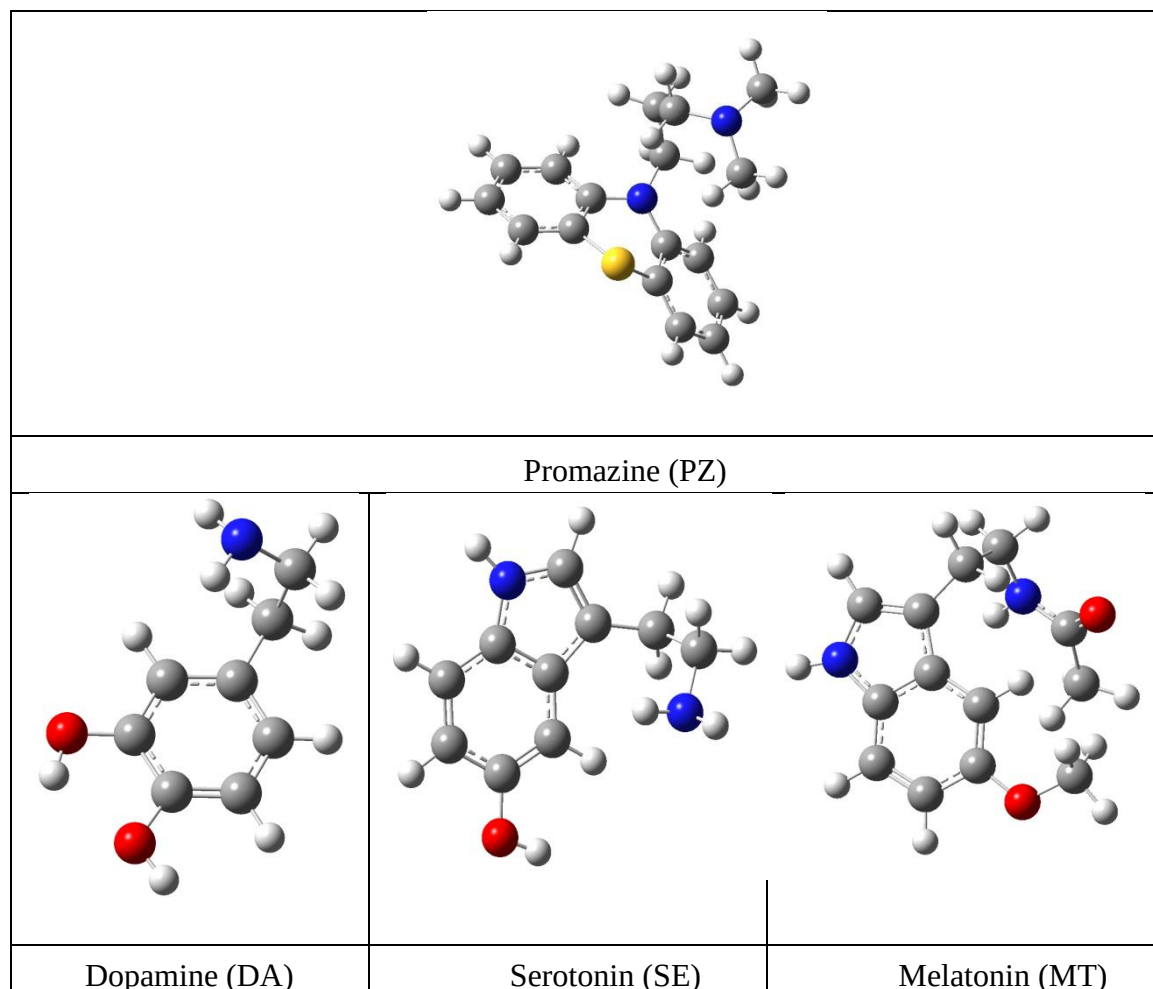


Figure 3.1. Optimized structures of the monomers of studied compounds

The properties of the used donor and acceptor systems are as follows: Promazine (98%, Sigma), Melatonin (98%, Sigma-Aldrich), Serotonin HCl (98%, Sigma-Aldrich), Dopamine HCl (Analytical, Fluka). Distilled water is used as solvent.

Sample solutions were treated to remove by bubbling through nitrogen for an extended period of time. The excitation wavelengths are chosen from UV-Vis absorption for all donor-acceptor complexes.

3.2 Methods

All absorbance spectra were measured using Perkin Elmer Lambda 35 UV/Vis Spectrophotometer and fluorescence measurements were performed by Perkin Elmer LS 55. The thickness of quartz cuvette is 1 cm.

Theoretical calculations were performed with Gaussian09, Gaussview 5.0 [46] and Spartan 08 [47] to investigate various physical properties of the molecules.

Specifically, DFT method used for this investigation. With the optimized geometries density functional theory (DFT) calculations were performed to examine and compare the energies and band gaps of molecules. For the DFT calculations the ω -B97XD functional was chosen with the 6-31G** basis set.

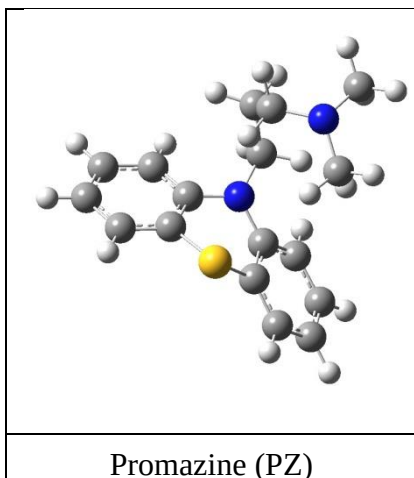
The excitation energies of molecules were calculated by the TD-DFT method, and the effects of electron donor and electron acceptor groups on the excitation energy as well as the orbital energies of HOMO and LUMO were examined.

Most studies of the fluorescence and absorption spectra and other photo physical properties of aromatic molecules are made in solution. The emitting or absorbing molecule is thus exposed to the influence of the surrounding molecules of the solvent, which can produce significant changes in its photophysical properties. The observed spectral and photophysical parameters are characteristic of the molecule in its solvent environment rather than of the isolated molecule [48].

Sample solutions were treated to remove by bubbling through nitrogen for an extended period of time. The excitation wavelengths are chosen from UV-Vis absorption for all donor-acceptor complexes.

These compounds used in the study are as given in figure 3.2:

Acceptors:



Donors:

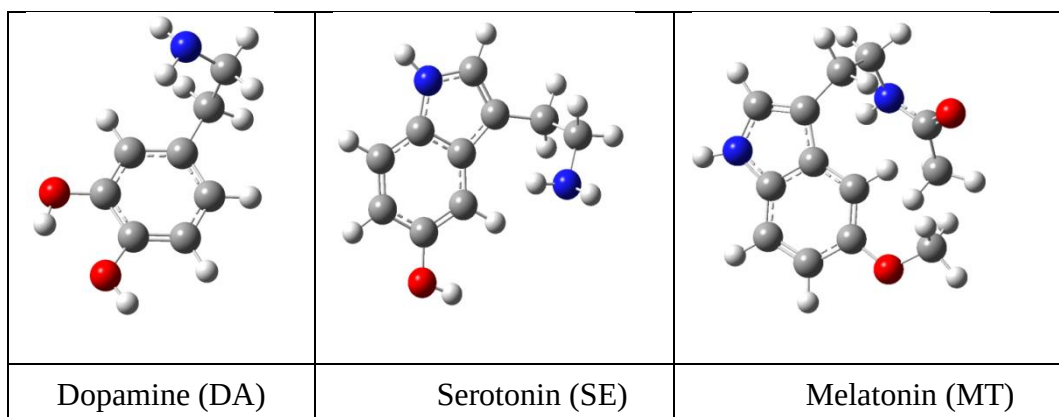


Figure 3.2. Molecular structure of donor and acceptor molecules.

4. RESULTS

4.1. Computational Investigations

4.1.1 Geometry Optimization

The geometries have been obtained by using Gaussian09, Gaussview5 and Spartan08 molecular modelling softwares. Ground state geometry optimizations are first performed at the ω -B97XD/6-31G(d,p) level of DFT theory without symmetry constraint.

Optimized bond lengths between the carbon atoms in the electronic ground state have been obtained at DFT (Figure 4.1). Electronic energies, dipole moments, zero point energies and relative energies of promazine and hormones(dopamine, serotonin and melatonin) in vacuum and in water are given in Tables 4.1 and 4.2. Table 4.3 shows calculated solvation free energies of studied promazine and hormones.

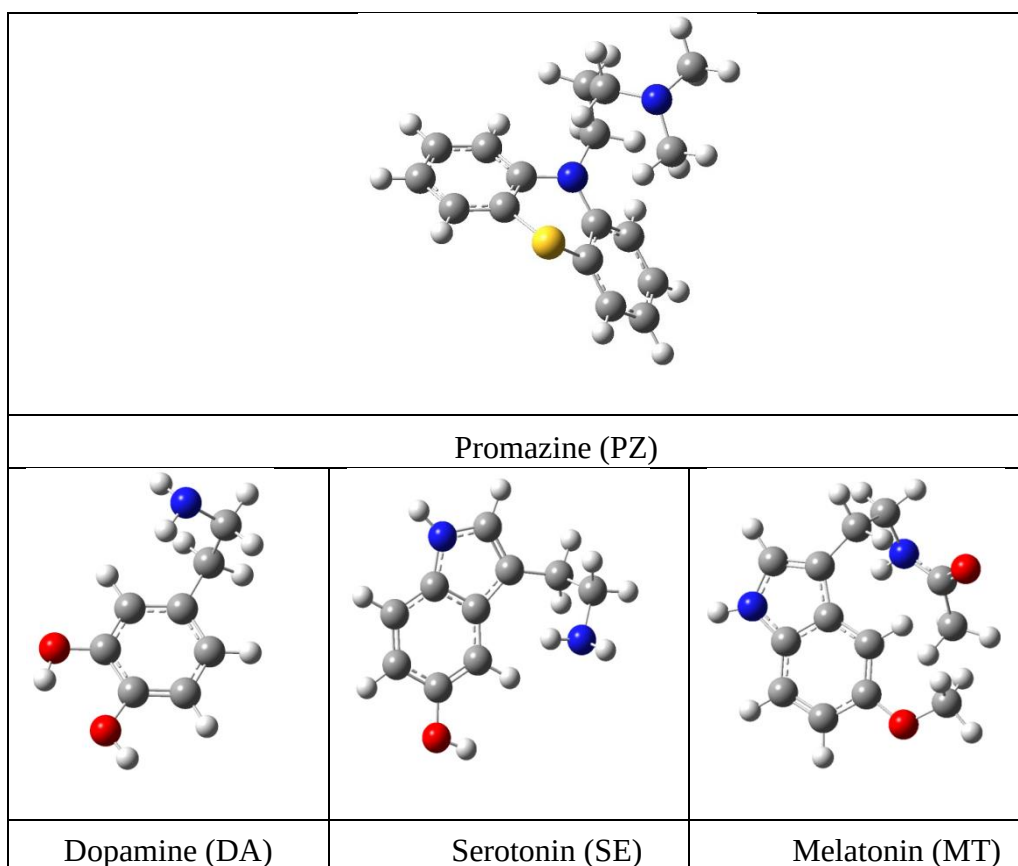


Figure 4.1. Optimized structures of the monomers of studied compounds.

Table 4.1. Calculated total electronic energies (E_{elec}), dipole moments (μ), zero-point energy corrections (ZPE), lowest frequencies (Freq), complexation energies (ΔE) and free energy differences ($\Delta\Delta G$) of studied compounds and their complexes in gas phase.

GAS	μ (D)	E_{elec} (Hartree)	ZPE (Hartree)	$E_{\text{elec}} + \text{ZPE}$ (Hartree)	$E_{\text{elec}} + \Delta G$ (Hartree)	Freq (cm^{-1})	ΔE (kcal/mol)	$\Delta\Delta G$ (kcal/mol)
PZ	2.36	-1167.3027	0.3419	-1166.9608	-1167.0063	33,74	-	-
DA	2.96	-516.5215	0.1858	-516.3357	-516.3723	51,93	-	-
SE	3.03	-572.8522	0.2117	-572.6405	-572.6774	71,39	-	-
MT	4.55	-764.7731	0.2790	-764.4940	-764.5370	41,27	-	-
PZ-DA	1.08	-1683.8532	0.5305	-1683.3226	-1683.3822	24,83	-16.41	-2.23
PZ-SE	2.02	-1740.1812	0.5560	-1739.6252	-1739.6869	15,49	-15.00	-4.13
PZ-MT	7.92	-1932.1056	0.6236	-1931.4820	-1931.5485	16,03	-18.69	-3.27

Table 4.2. Calculated total electronic energies (E_{elec}), dipole moments (μ), zero-point energy corrections (ZPE), lowest frequencies (Freq), complexation energies (ΔE) and free energy differences ($\Delta\Delta G$) of studied compounds and their complexes in water.

WATER	μ (D)	E_{elec} (Hartree)	ZPE (Hartree)	$E_{\text{elec}} + \text{ZPE}$ (Hartree)	$E_{\text{elec}} + \Delta G$ (Hartree)	Freq (cm^{-1})	ΔE (kcal/mol)	$\Delta\Delta G$ (kcal/mol)
PZ	3.65	-1167.3105	0.3422	-1166.9683	-1167.0130	35.95	-	-
DA	3.67	-516.5335	0.1855	-516.3481	-516.3824	49.91	-	-
SE	4.15	-572.8653	0.2116	-572.6536	-572.6905	62.40	-	-
MT	6.50	-764.7881	0.2787	-764.5094	-764.5525	41.34	-	-
PZ-DA	5.14	-1683.8663	0.5298	-1683.3364	-1683.3964	27.58	-14.01	-0.68
PZ-SE	3.08	-1740.2001	0.5555	-1739.6445	-1739.7064	18.95	-15.30	-1.86
PZ-MT	11.19	-1932.1234	0.6220	-1931.5013	-1931.5690	17.69	-15.60	-2.22

Table 4.3. Calculated solvation energies (E_{SOLV}) of studied promazine and hormones(dopamine, serotonin and melatonin).

Molecules	μ_v (D)	μ_s (D)	$E_{\text{SOLV}} = (E+\text{ZPE})_s - (E+\text{ZPE})_v$ (kcal/mol)
PZ	2.36	3.65	-4.89
DA	2.96	3.67	-7.53
SE	3.03	4.15	-8.22
MT	4.55	6.50	-9.41
PZ-DA	5.17	6.69	-8.67
PZ-SE	4.99	6.09	-12.16
PZ-MT	3.92	5.60	-12.14

Table 4.3 summarizes the solvation free energies for the studied systems. Free energy changes are not significant for molecules with small dipole moments in studied solvents.

The results indicate that promazine-melatonin (PZ-MT) complex is the most stable one in both media. However, the energy difference decreases in water. Free energy differences ($\Delta\Delta G$) indicate that promazine-serotonin (PZ-SE) complex forms easier in gas phase (Table 4.1) but promazine-melatonin (PZ-MT) complex forms easier in water (Table 4.2).

4.1.2 Electronic Transitions

Electronic structures (molecular orbitals and their energies) of electron donor and acceptor molecules have been calculated at ω -B97XD/6-31G** level with Density Functional Theory (DFT). The energy of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) transitions are shown for the molecules in gas phase and in water. Electron density plots for the HOMO and the LUMO orbitals at the

ground state and excited state equilibrium geometry of the compounds are shown for the complexes.

4.1.2.1 Promazine (PZ)

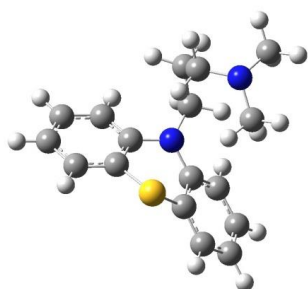


Figure 4.2. Optimized structure of promazine

Tables 4.4 and 4.5 display the electronic transitions (λ_{ex}), corresponding energy differences (ΔE), transition dipole moments ($\Delta\mu$), oscillator strengths (f), molecular orbitals and their % contributions of promazine (PZ) in gas phase and in water.

The main S_0 - S_1 transitions in both media occur from HOMO to LUMO (Table 4.4 and Table 4.5). The oscillator strengths are very small for lower transitions but they significantly increase at higher transitions. The differences are more drastic in gas phase.

Table 4.4. Excited state properties predicted by quantum chemical model calculations for promazine in gas phase.

PZ GAS	ΔE (eV)	λ (nm)	$\Delta\mu$ (D)	f	Predominant Transitions	%
S1	4.379	283.13	0.0038	0.0004	H-1 $\rightarrow$ L H $\rightarrow$ L	19 65
S2	4.730	262.15	0.2025	0.0235	H-4 $\rightarrow$ L H-3 $\rightarrow$ L+2 H -2 $\rightarrow$ L+3 H-1 $\rightarrow$ L+1 H $\rightarrow$ L+4	16 13 15 17 62
S3	4.841	256.13	0.6850	0.0812	H-4 $\rightarrow$ L+3 H-3 $\rightarrow$ L+1	13 17

					H-2→L H-1→L+2 H→L+2	24 18 60
S4	5.437	228.04	0.6250	0.0833	H-2→L H-2→L+1 H-1→L+3 H→L+2 H→L+3 H→L+4	17 19 15 11 57 15
S5	5.437	226.63	1.4655	0.1964	H-5→L+4 H-2→L H-2→L+4 H-1→L+4 H→L+2 H→L+3 H→L+4	10 37 19 13 17 26 38
S6	5.923	226.63	1.9337	0.2806	H-4→L+3 H-3→L+1 H-2→L H-2→L+4 H-1→L+4 H→L+2 H→L+4	10 12 40 13 13 21 43

Table 4.5. Excited state properties predicted by quantum chemical model calculations for promazine in water.

PZ H ₂ O	ΔE (eV)	λ (nm)	Δμ (D)	f	Predominant Transitions	%
S1	4.368	283.91	0.0230	0.0025	H-1→L H→L	14 66
S2	4.722	262.67	0.2990	0.0346	H-4→L H-3→L+2 H-2→L+3 H-1→L+1 H→L+1	15 13 14 13 64
S3	4.844	255.94	0.9972	0.1184	H-4→L+3 H-3→L+1 H-2→L H-1→L+2 H→L+2	12 17 22 13 61
S4	5.431	228.31	1.9962	0.2656	H-5→L+4 H-2→L H-2→L+4 H→L+2 H→L+3 H→L+4	10 41 18 19 24 36
S5	5.460	227.07	0.9935	0.1329	H-2→L H-2→L+1	16 18

					H-1 $\rightarrow$ L+3 H $\rightarrow$ L+3 H $\rightarrow$ L+4	10 59 17
S6	5.904	209.99	2.3489	0.3398	H-4 $\rightarrow$ L+3 H-3 $\rightarrow$ L H-3 $\rightarrow$ L+4 H-1 $\rightarrow$ L+4 H $\rightarrow$ L+2 H $\rightarrow$ L+4	11 40 15 10 19 46

4.1.2.2 Dopamine (DA)

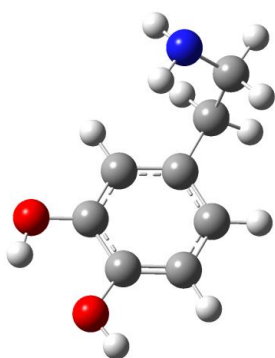


Figure 4.3. Optimized structure of dopamine

Table 4.6. Excited state properties predicted by quantum chemical model calculations for dopamine in gas phase.

DA GAS	ΔE (eV)	λ (nm)	$\Delta\mu$ (D)	f	Predominant Transitions	%
S1	5.173	239.68	0.4741	0.0601	H-2 $\rightarrow$ L+1 H $\rightarrow$ L	31 62
S2	5.962	207.97	0.3912	0.0571	H-2 $\rightarrow$ L H-1 $\rightarrow$ L H $\rightarrow$ L+1	32 12 61
S3	6.847	181.09	2.5356	0.4253	H-2 $\rightarrow$ L H-2 $\rightarrow$ L+1 H-1 $\rightarrow$ L H-1 $\rightarrow$ L+1 H $\rightarrow$ L H $\rightarrow$ L+1	50 18 12 30 18 26
S4	6.922	179.11	1.1390	0.1932	H-2 $\rightarrow$ L H-2 $\rightarrow$ L+1 H-1 $\rightarrow$ L H-1 $\rightarrow$ L+1 H $\rightarrow$ L	24 19 52 18 18

					H→L+1 H→ L+2	22 10
S5	6.931	178.88	0.0962	0.0163	H-2→ L H-2→L+2 H-1→L+2 H→L+2	12 13 11 64
S6	7.102	174.58	2.0388	0.3547	H-2→ L H-2→L+1 H-1→L H →L+1 H→ L	23 40 42 25 17

Tables 4.6 and 4.7 displays the electronic transitions (λ_{ex}), corresponding energy differences (ΔE), transition dipole moments ($\Delta\mu$), oscillator strengths (f), molecular orbitals and their % contributions of dopamine in gas phase and in water.

The main S_0 - S_1 transitions in both media occur from HOMO to LUMO similar to promazine (Table 4.6 and Table 4.7). The oscillator strengths are very small for almost all transitions in contrast to the observed values for promazine.

Table 4.7. Excited state properties predicted by quantum chemical model calculations for dopamine in water.

DA H ₂ O	ΔE (eV)	λ (nm)	$\Delta\mu$ (D)	f	Predominant Transitions	%
S1	5.158	240.37	0.5891	0.0744	H-1→ L+1 H →L	31 63
S2	5.931	209.04	0.5771	0.0839	H-1 → L H→ L+1	32 62
S3	6.790	182.61	3.3825	0.5626	H-1→L H-1→L+1 H→L+1	60 16 31
S4	6.907	179.50	3.9148	0.6625	H -2→ L H-1→L H-1 → L+1 H→L	10 17 59 30
S5	7.239	171.28	0.2157	0.0383	H-2→L H-2→ L+1 H-1→ L+1	64 20 14
S6	7.280	170.31	0.0214	0.0038	H-2 → L H-2→L+1 H→L+4	11 66 11

4.1.2.3. Serotonin (SE)

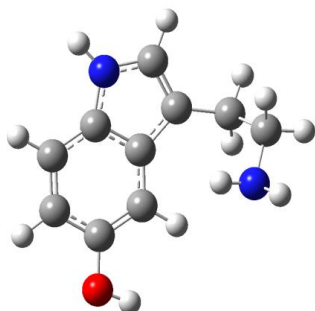


Figure 4.4. Optimized structure of serotonin

Tables 4.8 and 4.9 display the corresponding electronic transitions (λ_{ex}) for serotonin (SE) in gas phase and in water, respectively. The main S_0 - S_1 transitions in both media occur from HOMO to LUMO similar to promazine and dopamine (Table 4.8 and Table 4.9). The oscillator strengths are very small for almost all transitions like in dopamine but in contrast to promazine values.

Table 4.8. Excited state properties predicted by quantum chemical model calculations for serotonin in gas phase.

SE GAS	ΔE (eV)	λ (nm)	$\Delta\mu$ (D)	f	Predominant Transitions	%
S1	4.787	259.00	0.722	0.084	H-1 $\rightarrow$ L H-1 $\rightarrow$ L+1 H $\rightarrow$ L H $\rightarrow$ L+1	25 18 62 10
S2	5.198	238.54	0.821	0.104	H-1 $\rightarrow$ L H $\rightarrow$ L H $\rightarrow$ L-1	59 28 25
S3	6.537	189.66	3.665	0.587	H-3 $\rightarrow$ L H-1 $\rightarrow$ L H $\rightarrow$ L+1	16 25 63
S4	6.642	186.66	0.904	0.147	H-3 $\rightarrow$ L H-2 $\rightarrow$ L H-1 $\rightarrow$ L+1 H $\rightarrow$ L	21 14 63 15
S5	6.906	179.54	0.244	0.041	H-2 $\rightarrow$ L H-1 $\rightarrow$ L+1 H $\rightarrow$ L+2	65 15 14

S6	7.087	174.95	1.127	0.195	H-3→L	39
					H-2→L	18
					H-1→L	11
					H→L+2	51

Table 4.9. Excited state properties predicted by quantum chemical model calculations for serotonin in water.

SE H ₂ O	ΔE (eV)	λ (nm)	Δμ (D)	f	Predominant Transitions	%
S1	4.760	260.45	0.8389	0.0978	H-1→L	29
					H-1→L+1	16
					H→L	61
					H→L+1	11
S2	5.094	243.38	1.1311	0.1412	H-1→L	58
					H→L	32
					H→L+1	23
S3	6.396	193.85	5.1113	0.8009	H-1→L	26
					H→L+1	64
S4	6.574	188.59	0.7761	0.1250	H-3→L	21
					H-2→L	10
					H-1→L+1	64
					H→L	17
S5	6.9086	179.46	0.2883	0.0488	H-3→L	17
					H-2→L	64
					H-1→L+1	13
					H→L+2	17
S6	7.080	175.11	0.7984	0.1385	H-3→L	47
					H-2→L	26
					H→L+2	42

4.1.2.4. Melatonin (MT)

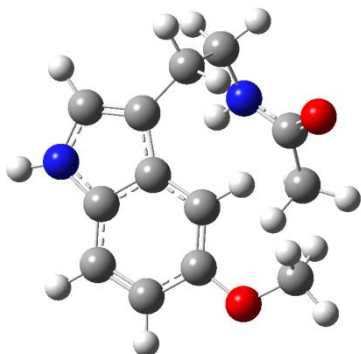


Figure 4.5. Optimized structure of melatonin

Tables 4.10 and 4.11 display the corresponding electronic transitions (λ_{ex}) for melatonin (MT) in gas phase and in water, respectively. The main S_0 - S_1 transitions in both media occur from HOMO to LUMO similar to promazine, dopamine and serotonin (Table 4.10 and Table 4.11). The oscillator strengths are very small for almost all transitions like in dopamine and serotonin but in contrast to promazine values.

Table 4.10. Excited state properties predicted by quantum chemical model calculations for melatonin in gas phase.

MT GAS	ΔE (eV)	λ (nm)	$\Delta\mu$ (D)	f	Predominant Transitions	%
S1	4.796	258.52	0.6736	0.0791	H-1 $\rightarrow$ L H-1 $\rightarrow$ L+1 H-1 $\rightarrow$ L+2 H $\rightarrow$ L	19 13 15 63
S2	5.210	237.95	0.8130	0.1038	H-1 $\rightarrow$ L H $\rightarrow$ L H $\rightarrow$ L+1 H $\rightarrow$ L+2	62 22 17 17
S3	5.707	217.27	0.0210	0.0029	H-3 $\rightarrow$ L+1 H-3 $\rightarrow$ L+2 H-2 $\rightarrow$ L+1 H-2 $\rightarrow$ L+2	28 21 48 34
S4	6.432	192.75	3.2387	0.5104	H-4 $\rightarrow$ L H-1 $\rightarrow$ L H $\rightarrow$ L+1 H $\rightarrow$ L+2	13 23 54 34
S5	6.575	188.58	1.1433	0.1842	H-4 $\rightarrow$ L H-1 $\rightarrow$ L+1 H-1 $\rightarrow$ L+1 H $\rightarrow$ L+2 H $\rightarrow$ L+1	12 52 38 18 11
S6	6.868	180.52	0.4719	0.0794	H-3 $\rightarrow$ L+1 H-1 $\rightarrow$ L+2 H $\rightarrow$ L+1 H $\rightarrow$ L+2 H $\rightarrow$ L+3	12 22 34 52 11

Table 4.11 Excited state properties predicted by quantum chemical model calculations for melatonin in water.

MT H ₂ O	ΔE (eV)	λ (nm)	$\Delta\mu$ (D)	f	Predominant Transitions	%
S1	4.787	258.90	0.7787	0.0913	H-1 $\rightarrow$ L H-1 $\rightarrow$ L+2 H $\rightarrow$ L	31 14 60
S2	5.093	243.40	1.1508	0.1436	H -1 $\rightarrow$ L H $\rightarrow$ L H $\rightarrow$ L+1 H $\rightarrow$ L+2	57 34 13 17
S3	5.852	211.85	0.0217	0.0031	H-3 $\rightarrow$ L+1 H-3 $\rightarrow$ L+2 H-2 $\rightarrow$ L+1 H-2 $\rightarrow$ L+2	41 27 41 26
S4	6.340	195.55	4.6544	0.7230	H-1 $\rightarrow$ L H $\rightarrow$ L+1 H $\rightarrow$ L+2	24 50 42
S5	6.487	191.13	1.0942	0.1739	H-4 $\rightarrow$ L H-1 $\rightarrow$ L+1 H-1 $\rightarrow$ L+1 H $\rightarrow$ L	14 48 44 15
S6	6.792	182.54	0.2454	0.0408	H-3 $\rightarrow$ L+1 H-1 $\rightarrow$ L+2 H $\rightarrow$ L+1 H $\rightarrow$ L+2	12 13 44 50

The frontier molecular orbitals (MOs) of electronically excited states of studied molecules are displayed in Figure 4.6. Both HOMO and LUMO are located mostly on the rings for all studied monomers. This observation is valid for orbitals both in gas phase and in water. The results displayed for promazine and the hormones (Dopamine, Serotonin and Melatonin) indicate that there are no significant changes in the properties and molecular orbitals in gas phase and in water. Also, electron transition is easier in water than in gas phase.

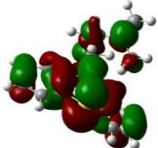
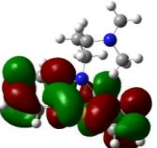
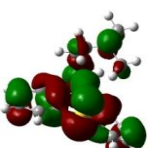
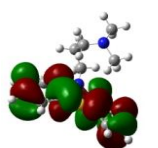
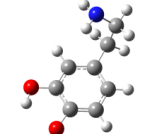
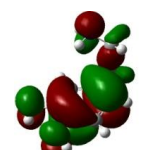
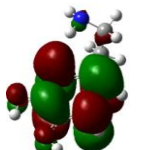
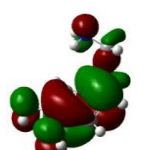
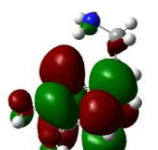
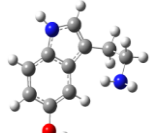
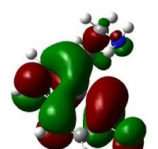
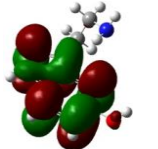
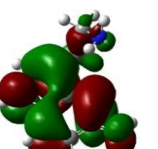
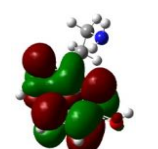
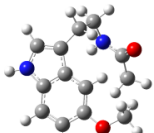
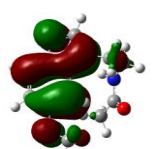
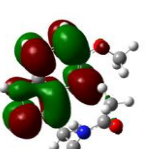
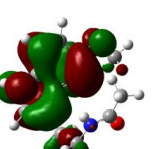
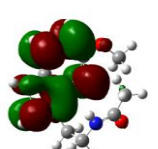
	GAS PHASE		ΔE	WATER		ΔE
	HOMO	LUMO		HOMO	LUMO	
 Promazine			4.379 eV			4.367 eV
 Dopamine			5.172 eV			5.158 eV
 Serotonin			4.787 eV			4.760 eV
 Melatonin			4.796 eV			4.787 eV

Figure 4.6. Frontier molecular orbitals of studied molecules involved in the CI-description of lowest excited singlet states (in gas phase and in water)

4.1.3 Promazine and Hormone (Dopamine, Serotonin and Melatonin) Systems

4.1.3.1 Promazine-Dopamine

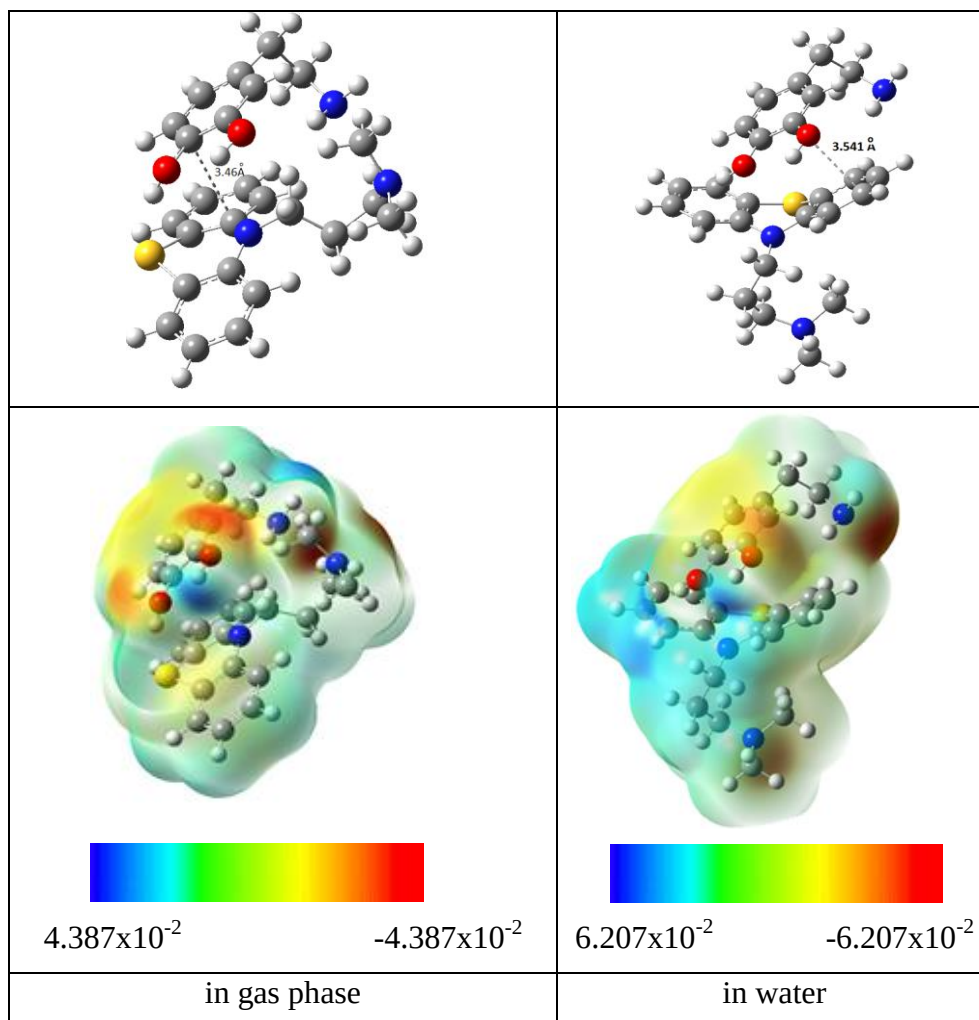


Figure 4.7. Optimized structures of promazine- dopamine complexes in gas phase and in water

Promazine-dopamine complexes have different geometries in gas phase and in water (Figure 4.7). The aromatic ring of dopamine is always oriented towards the isoalloxazine ring of promazine but the orientation of the -NH_2 terminal group changes in water as it is directed towards the ring part of promazine rather than the $\text{-N(CH}_3)_2$ group as in gas phase.

When electronic excitations are examined in gas phase (Table 4.12), it is observed that the $S_0 \rightarrow S_1$ transition is a local excitation of promazine

(LE1) (Figure 4.8). The first charge transfer from promazine to dopamine (CT1) is observed at $S_0 \rightarrow S_3$ from H-4 and H-3 to L. However, its magnitude is low and the main process is LE1. At $S_0 \rightarrow S_4$, both charge transfer from promazine to dopamine (CT1) and charge transfer from dopamine to promazine (CT2) are observed. Although, there are slight local excitations (LE1) observed, the main processes are CT1 and CT2, former predominating. Both $S_0 \rightarrow S_5$ and $S_0 \rightarrow S_6$ transitions have mainly charge transfer character. It is clearly seen that charge transfer increases significantly at higher transitions in gas phase.

Table 4.12. Excited state properties predicted by quantum chemical model calculations for promazine- dopamine system in gas phase.

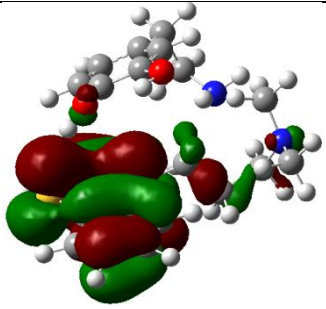
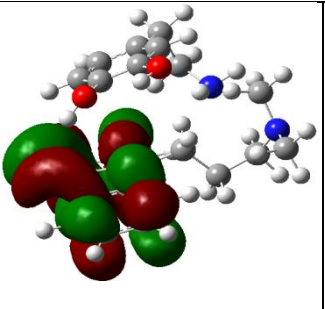
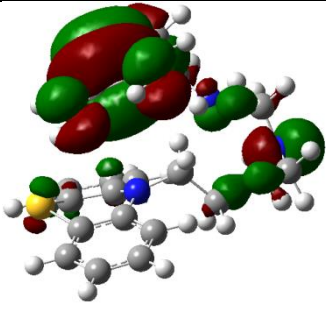
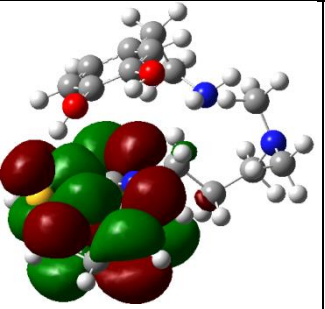
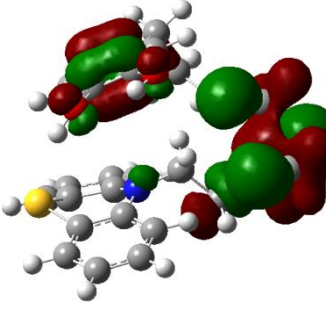
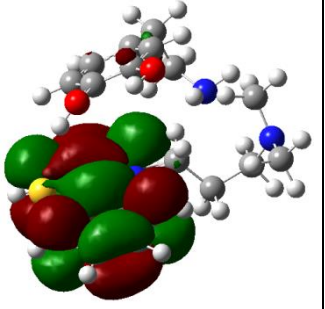
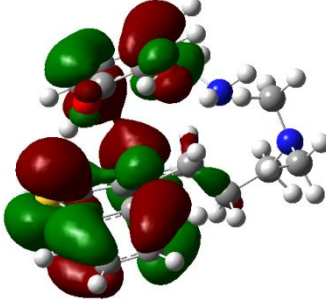
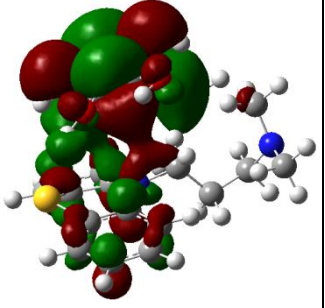
PZ-DA	ΔE (eV)	λ (nm)	$\Delta\mu$ (D)	f	Character	Predominant Transitions	%
S1	4.045	306.50	0.1404	0.0139	LE1	H $\rightarrow$ L	68
S2	4.624	268.12	0.2176	0.0247	LE1	H-7 $\rightarrow$ L H-6 $\rightarrow$ L+2 H $\rightarrow$ L+1	16 13 65
S3	4.729	262.16	0.6113	0.0708	CT1+LE1 CT1+LE1 LE1	H-6 $\rightarrow$ L+1 H-4 $\rightarrow$ L H-3 $\rightarrow$ L H $\rightarrow$ L+2	13 12 22 61
S4	5.099	243.18	0.2101	0.0262	LE1+CT1 CT1+LE1 CT1+CT2 CT2+	H-4 $\rightarrow$ L+4 H-4 $\rightarrow$ L+5 H-3 $\rightarrow$ L+4 H-2 $\rightarrow$ L+3 H-1 $\rightarrow$ L+3 H-1 $\rightarrow$ L+5	22 13 15 19 56 16
S5	5.352	231.64	1.8340	0.2405	CT2+LE1 CT2+LE1 CT2+LE1 LE1 LE1	H-4 $\rightarrow$ L H-3 $\rightarrow$ L H-3 $\rightarrow$ L+6 H-1 $\rightarrow$ L H $\rightarrow$ L H $\rightarrow$ L+2 H $\rightarrow$ L+6	15 29 16 18 11 20 46
S6	5.568	222.65	0.3324	0.0454	CT2+LE1 CT2 CT2 LE1+CT1 LE1+CT1	H-7 $\rightarrow$ L+2 H-3 $\rightarrow$ L+1 H-1 $\rightarrow$ L H-1 $\rightarrow$ L+1 H $\rightarrow$ L+3 H $\rightarrow$ L+4 H $\rightarrow$ L+5	11 17 14 11 50 18 31

LE1: locally excited promazine

LE2: locally excited dopamine

CT1: charge transfer from promazine to dopamine

CT2: charge transfer from dopamine to promazine

	HOMO -7.07 eV		LUMO 1.17 eV
	H - 1 -7.43 eV		L + 1 1.50 eV
	H - 2 -7.73 eV		L + 2 1.69 eV
	H - 3 -8.52 eV		L + 3 2.00 eV

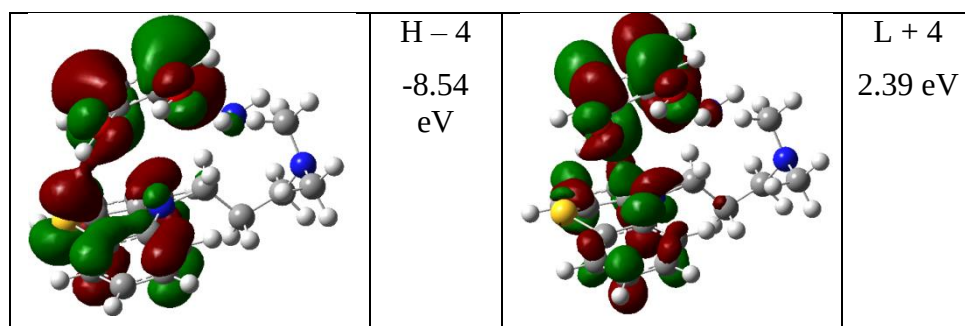


Figure 4.8. Frontier molecular orbitals of promazine-dopamine system in gas phase involved in the CI-description of lowest excited singlet states

Table 4.13 and Figure 4.9 display the molecular orbitals and excited properties of promazine-dopamine system calculated in water. In contrast to gas phase, the $S_0 \rightarrow S_1$ transition corresponds to charge transfer from dopamine to promazine (CT2) accompanied by a locally excited promazine (LE1) (Table 4.13). $H \rightarrow L+1$ transition is the most abundant one (51%). In all other transitions except $S_0 \rightarrow S_3$ charge transfer is the main process, but $S_0 \rightarrow S_3$ transition has been mostly dominated by locally excited promazine (LE1) and dopamine (LE2).

Table 4.13. Excited state properties predicted by quantum chemical model calculations for promazine-dopamine system in water.

PZ-DA	ΔE (eV)	λ (nm)	$\Delta\mu$ (D)	f	Character	Predominant Transitions	%
S1	4.332	286.19	0.0245	0.0026	LE1+CT2	H-2 $\rightarrow$ L	11
					LE1+CT2	H-2 $\rightarrow$ L+1	13
					LE1	H $\rightarrow$ L	42
					LE1+CT2	H $\rightarrow$ L+1	51
S2	4.593	269.93	0.4854	0.0546		H-7 $\rightarrow$ L+1	10
						H-6 $\rightarrow$ L	11
					LE1+CT2	H-2 $\rightarrow$ L	14
					LE1+CT2	H $\rightarrow$ L	49
S3	4.759	260.52	0.6973	0.0813	LE1+CT2	H $\rightarrow$ L+1	41
						H-6 $\rightarrow$ L+2	11
					LE1+CT2	H-3 $\rightarrow$ L+1	14
					LE1+LE2	H-2 $\rightarrow$ L+2	13
S4	5.136	241.43	0.3529	0.0444	LE1+LE2	H $\rightarrow$ L+2	62
						H-4 $\rightarrow$ L+5	27
					LE1+CT2	H-2 $\rightarrow$ L+2	10
					LE1+CT1	H-2 $\rightarrow$ L+4	19
					LE1+CT2	H-1 $\rightarrow$ L+2	21

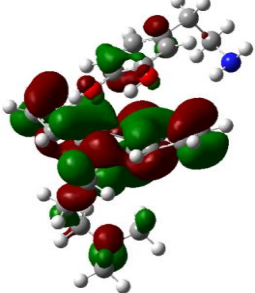
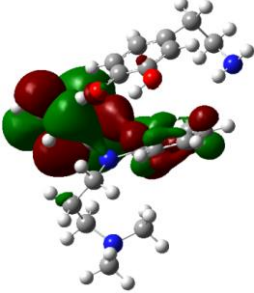
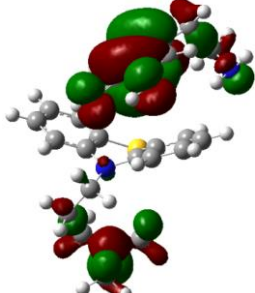
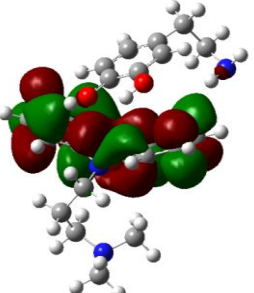
					LE1+CT2	H-1 $\rightarrow$ L+3	21
					LE1+CT2	H-1 $\rightarrow$ L+4	46
					CT2	H $\rightarrow$ L+4	16
					+LE1		
S5	5.395	229.80	1.1683	0.1544	CT2	H-3 $\rightarrow$ L	16
					CT2	H-3 $\rightarrow$ L+1	36
						H-3 $\rightarrow$ L+6	16
					LE1+LE2	H $\rightarrow$ L+2	16
					LE1+CT2	H $\rightarrow$ L+3	25
					LE1+CT2	H $\rightarrow$ L+4	12
						H $\rightarrow$ L+6	34
S6	5.440	227.92	0.8609	0.1147	CT1	H-3 $\rightarrow$ L	23
					LE1+CT1	H-2 $\rightarrow$ L+3	11
					LE1+CT1	H $\rightarrow$ L+3	54
					LE1+CT1	H $\rightarrow$ L+4	17
						H $\rightarrow$ L+6	20

LE1: locally excited promazine

LE2: locally excited dopamine

CT1: charge transfer from promazine to dopamine

CT2: charge transfer from dopamine to promazine

	HOMO -7.18 eV		LUMO 1.25 eV
	H - 1 -7.54 eV		L + 1 1.31 eV

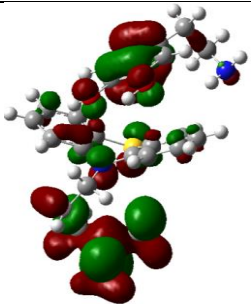
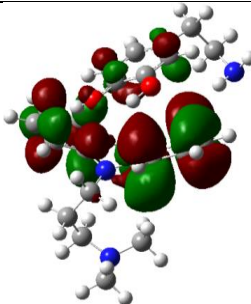
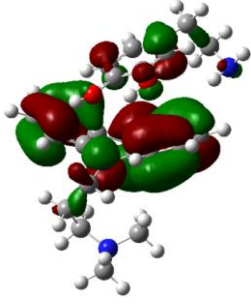
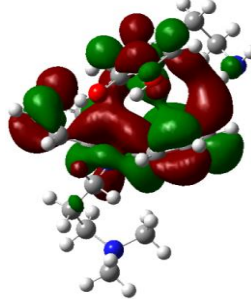
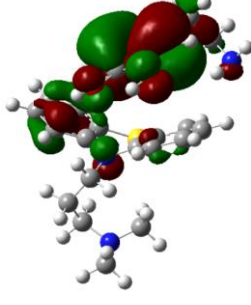
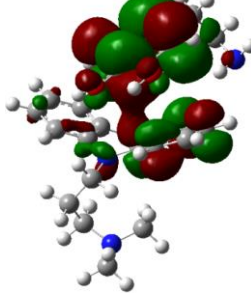
	H - 2 -7.59 eV		L+2 1.55 eV
	H - 3 -8.30 eV		L + 3 1.96 eV
	H - 4 -8.46 eV		L+4 2.07 eV

Figure 4.9. Frontier molecular orbitals of promazine-dopamine system in water involved in the CI-description of lowest excited singlet states

4.1.3.2 Promazine-Serotonin

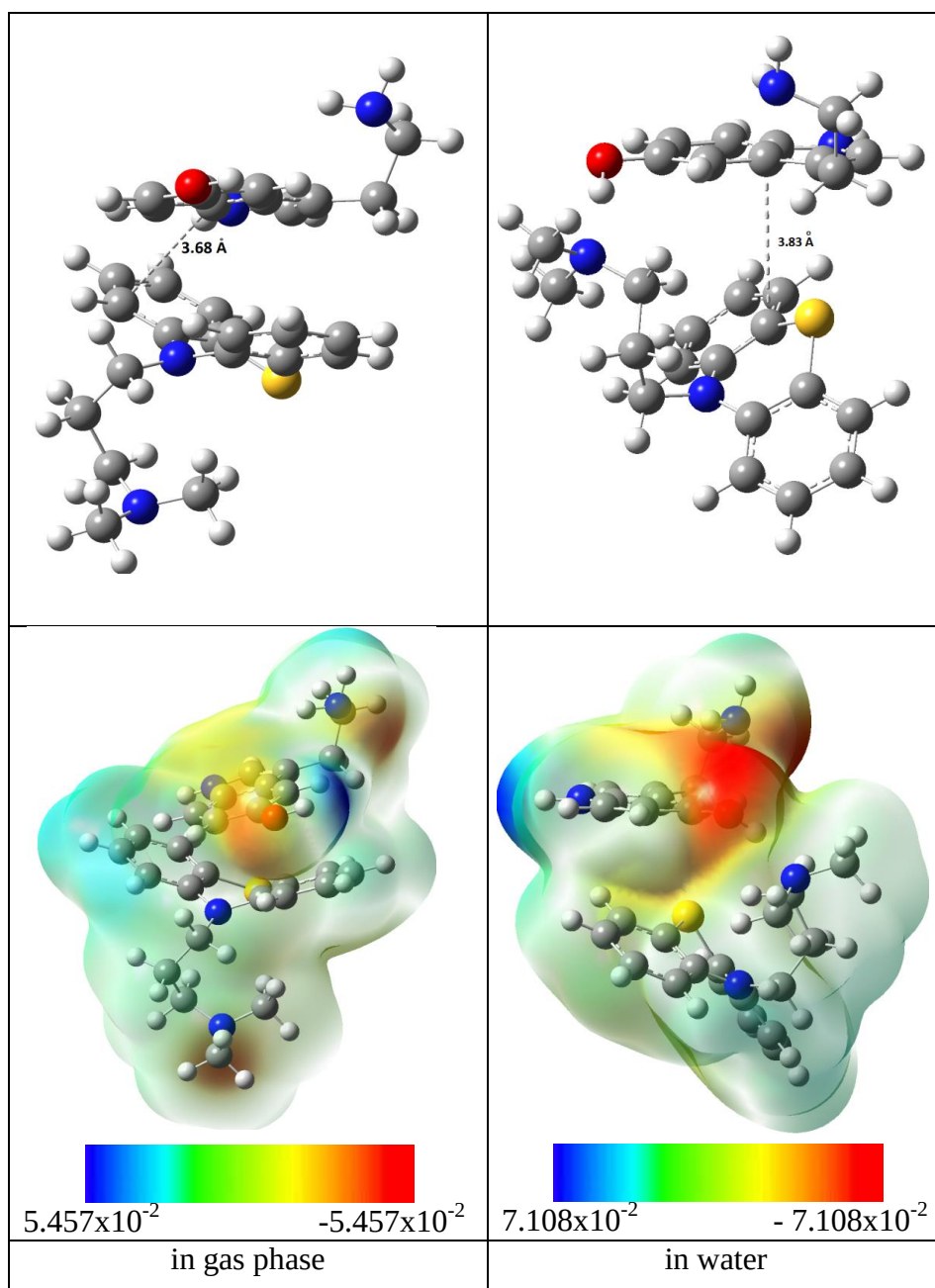


Figure 4.10. Optimized structures of promazine-serotonin complexes in gas phase and in water

Promazine-serotonin complexes have also different geometries in gas phase and in water (Figure 4.10). The aromatic rings of promazine and serotonin face each other in gas phase but the orientation of the –OH side chain on the phenyl ring of serotonin directed towards the –N(CH₃)₂ group

in water. Slight distortion of the OH hydrogen may indicate presence of a hydrogen bonding.

When electronic excitations are examined in gas phase (Table 4.14), it is observed that the $S_0 \rightarrow S_1$ transition is a mixture of charge transfer from promazine to serotonin (CT1), charge transfer from serotonin to promazine (CT2), locally excited promazine (LE1), and locally excited serotonin (LE2) (Figure 4.11). The main contribution comes from H-1 $\rightarrow$ L (55%) which corresponds to LE1+CT1. The results are similar for other higher transitions. It may be concluded that promazine-serotonin system has a tendency for charge transfer in gas phase in contrast to the promazine-dopamine system.

Table 4.14. Excited state properties predicted by quantum chemical model calculations for promazine-serotonin system in gas phase.

PZ-SE	ΔE (eV)	λ (nm)	$\Delta\mu$ (D)	f	Character	Predominant Transitions	%
S1	4.278	289.85	0.0223	0.0023	CT1+LE1	H-3 $\rightarrow$ L	18
					LE1+CT1	H-1 $\rightarrow$ L	55
					CT2+LE1	H-1 $\rightarrow$ L+1	29
					CT2+LE2	H $\rightarrow$ L	14
S2	4.600	269.52	0.3134	0.0353	LE1	H-3 $\rightarrow$ L+1	17
					LE1+CT1	H-1 $\rightarrow$ L	26
					CT2+LE1	H-1 $\rightarrow$ L+1	53
					CT1+LE1	H-1 $\rightarrow$ L+2	10
					CT2+LE2	H $\rightarrow$ L	11
					CT2	H $\rightarrow$ L+1	11
S3	4.685	264.65	0.4280	0.0491	CT2+LE2	H-2 $\rightarrow$ L+2	21
					CT2+LE2	H-2 $\rightarrow$ L+3	11
						H-2 $\rightarrow$ L+5	14
					LE1+CT1	H-1 $\rightarrow$ L	13
					CT2+LE1	H-1 $\rightarrow$ L+1	10
					LE2+CT2	H $\rightarrow$ L	25
					LE2+CT2	H $\rightarrow$ L+2	42
					LE2+CT2	H $\rightarrow$ L+3	30
					LE2+CT2	H $\rightarrow$ L+4	10
S4	4.805	258.03	0.3350	0.0394	CT1+LE2	H-4 $\rightarrow$ L	13
					CT2	H-4 $\rightarrow$ L+1	10
					LE1+LE2	H-4 $\rightarrow$ L+4	14
					CT1+LE1	H-3 $\rightarrow$ L-2	11
					CT1+LE1	H-3 $\rightarrow$ L-3	12
					LE1+CT1	H-1 $\rightarrow$ L+2	41

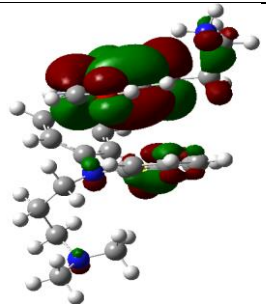
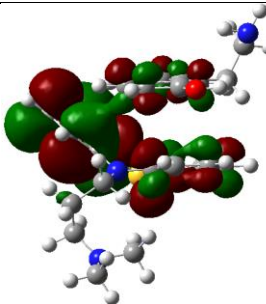
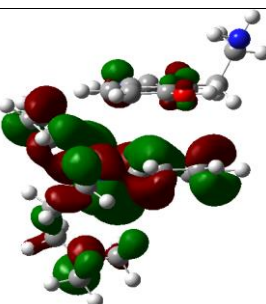
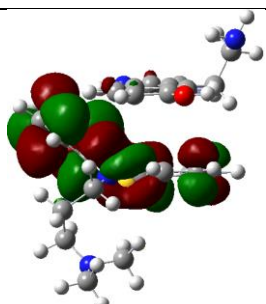
					LE1+CT1	H-1 → L+3	40
					CT2+LE2	H → L+2	13
					CT2+LE2	H → L+3	13
S5	4.996	248.16	0.3271	0.0400	CT2+LE2	H-2 → L	27
					CT2+LE2	H-2 → L+2	43
					CT2+LE2	H-2 → L+3	27
					CT2+LE2	H → L	19
					CT2+LE2	H → L+2	24
					CT2+LE2	H → L+6	21
S6	5.315	233.28	0.6057	0.0789	LE2+CT1	H-4 → L+1	12
					CT1+LE1	H-1 → L	12
					CT2+LE1	H-1 → L+1	14
					CT1+LE1	H-1 → L+2	18
						H-1 → L+5	14
					CT2+LE2	H → L	39
					CT2	H → L+1	34
					CT2+LE2	H → L+2	13
					CT2+LE2	H → L+3	12
					CT2+LE2	H → L+4	17

LE1: locally excited promazine

LE2: locally excited serotonin

CT1: charge transfer from promazine to serotonin

CT2: charge transfer from serotonin to promazine

	HOMO -6.97 eV		LUMO 1.31 eV
	H - 1 -7.05 eV		L + 1 1.50 eV

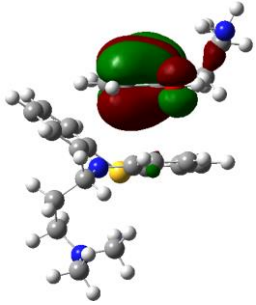
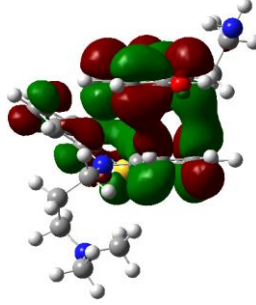
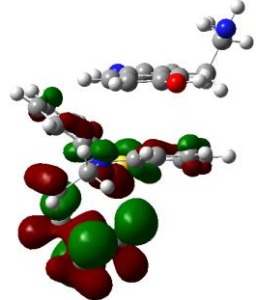
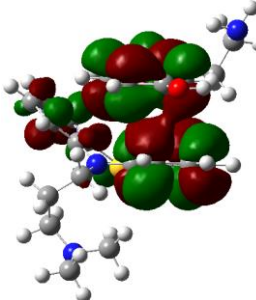
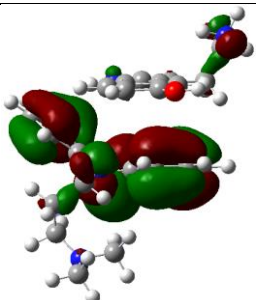
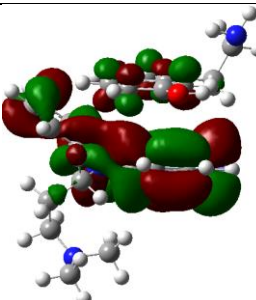
	H - 2 -7.27 eV		L + 2 1.69 eV
	H - 3 -7.35 eV		L + 3 1.90 eV
	H - 4 -8.11 eV		L + 4 2.23 eV

Figure 4.11. Molecular orbitals of promazine-serotonin system in gas phase involved in the CI-description of lowest excited singlet states

Table 4.15 and Figure 4.12 display the molecular orbitals and excited state properties of promazine-serotonin system calculated in water. In water, CT2 disappears for the $S_0 \rightarrow S_1$ transition and the main transition from $H \rightarrow L$ corresponds to a mixture of LE1+LE2 (64%) (Table 4.15). In other transitions CT and LE states are separated more significantly compared to gas phase. Results in water also indicate that promazine-serotonin system has more tendency for charge transfer compared to promazine-dopamine system.

Table 4.15. Excited state properties predicted by quantum chemical model calculations for promazine-serotonin system in water.

PZ-SE	ΔE (eV)	λ (nm)	$\Delta\mu$ (D)	f	Character	Predominant Transitions	%
S1	4.199	295.26	0.0608	0.0063	CT1 LE1+LE2 CT1+LE1	H-1 $\rightarrow$ L H $\rightarrow$ L H $\rightarrow$ L+2	17 64 12
S2	4.592	269.96	0.2231	0.0251	LE1 CT1 CT2+LE1 LE1+LE2 CT1	H-7 $\rightarrow$ L H-6 $\rightarrow$ L+3 H-3 $\rightarrow$ L+4 H-1 $\rightarrow$ L+1 H-1 $\rightarrow$ L+2 H $\rightarrow$ L+1 H $\rightarrow$ L+2	14 11 12 13 11 61 14
S3	4.688	264.45	0.5006	0.0575	CT2 CT2 CT2 LE1+CT2 CT2 CT1	H-2 $\rightarrow$ L+2 H-2 $\rightarrow$ L+6 H-1 $\rightarrow$ L H-1 $\rightarrow$ L+1 H-1 $\rightarrow$ L+2 H-1 $\rightarrow$ L+3 H $\rightarrow$ L+2	20 14 21 17 50 18 19
S4	4.738	261.65	1.0836	0.1258	LE1 LE1+CT2 CT2 CT1 LE1+LE2	H-7 $\rightarrow$ L+4 H-6 $\rightarrow$ L+1 H-3 $\rightarrow$ L H-1 $\rightarrow$ L+2 H-1 $\rightarrow$ L+3 H $\rightarrow$ L+2 H $\rightarrow$ L+3	12 16 20 11 13 21 57
S5	5.082	243.94	0.8411	0.1047	CT2 CT2 CT2+LE2 CT2+LE2 CT1 LE1+CT2	H-2 $\rightarrow$ L H-2 $\rightarrow$ L+1 H-2 $\rightarrow$ L+2 H-2 $\rightarrow$ L+3 H-1 $\rightarrow$ L+1 H-1 $\rightarrow$ L+2 H-1 $\rightarrow$ L+5 H-1 $\rightarrow$ L+6	19 17 52 26 12 22 10 19
S6	5.324	232.88	0.6924	0.0903	CT2 CT2 CT1+LE1 CT2	H-3 $\rightarrow$ L+1 H-1 $\rightarrow$ L+4 H $\rightarrow$ L+2 H $\rightarrow$ L+4	16 15 15 62

LE1: locally excited promazine

LE2: locally excited serotonin

CT1: charge transfer from promazine to serotonin

CT2: charge transfer from serotonin to promazine

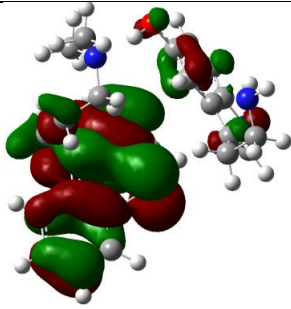
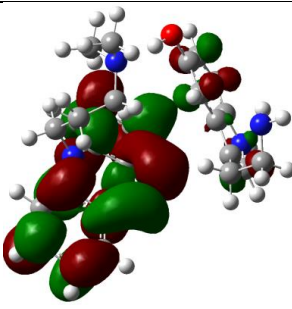
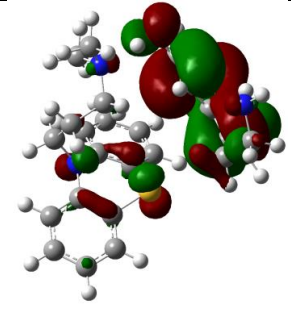
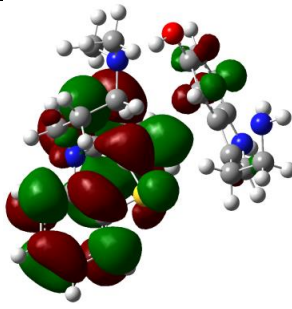
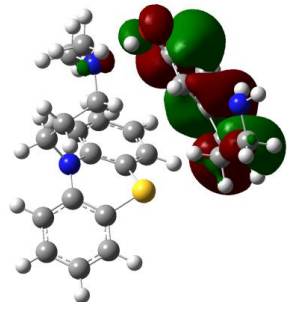
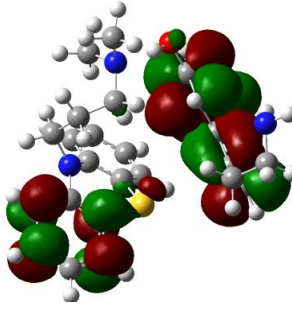
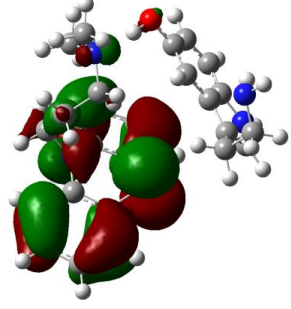
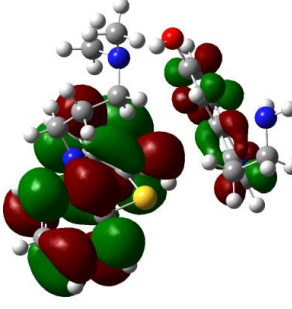
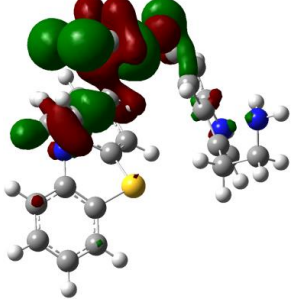
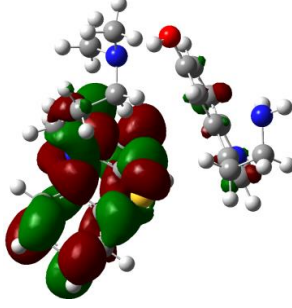
	HOMO -7.05 eV		LUMO 1.33 eV
	H - 1 -7.13 eV		L + 1 1.52 eV
	H - 2 -7.43 eV		L + 2 1.61 eV
	H - 3 -8.16 eV		L + 3 1.74 eV
	H - 4 -8.41 eV		L + 4 2.10 eV

Figure 4.12. Molecular orbitals of promazine-serotonin system in water involved in the CI-description of lowest excited singlet states

4.1.3.3 Promazine-Melatonin

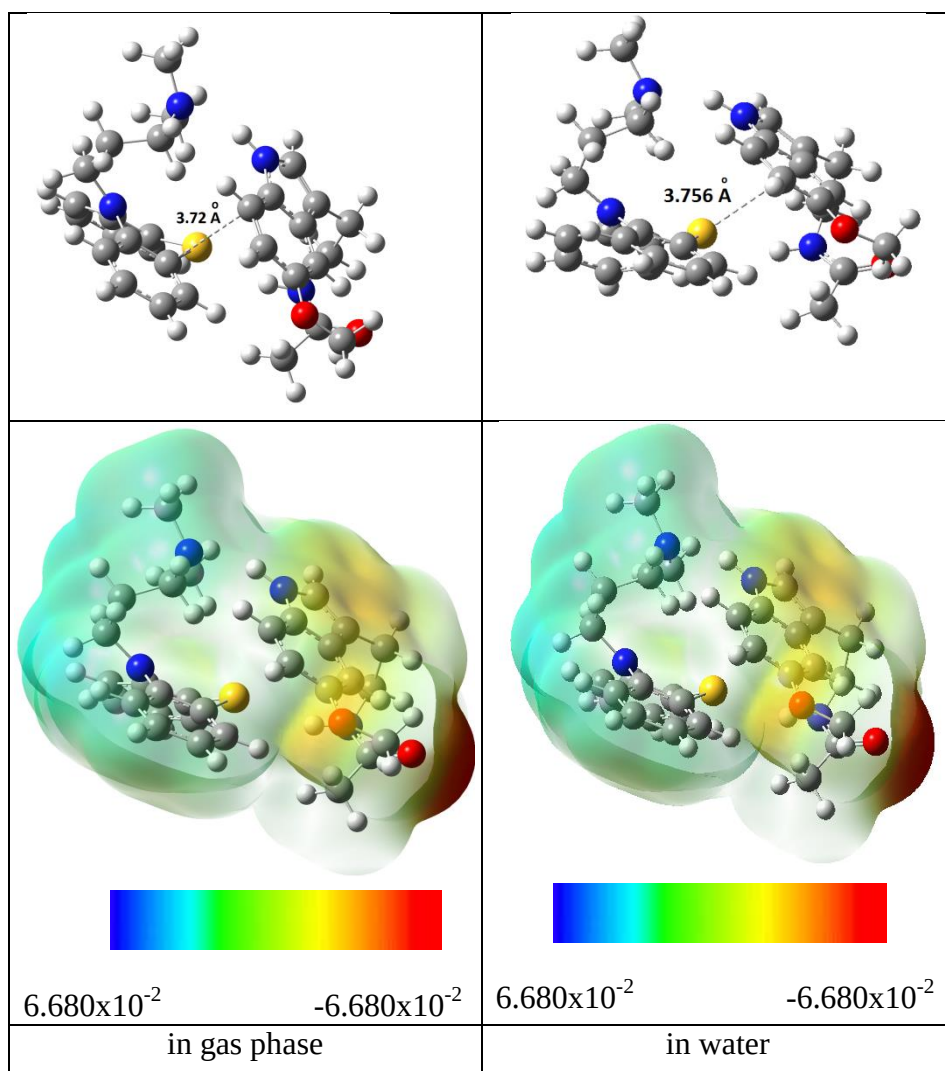


Figure 4.13. Optimized structures of promazine-melatonin complexes in gas phase and in water

In contrast to former two systems, promazine-melatonin complexes have similar geometries in gas phase and in water (Figure 4.13). The aromatic rings of promazine and melatonin face each other both in gas phase and in water. Although there is a slight distortion in the complex geometry, the general structure remains the same.

When electronic excitations are examined in gas phase (Table 4.16), it is observed that the $S_0 \rightarrow S_1$ transition is a mixture of charge transfer from melatonin to promazine (CT2), locally excited promazine (LE1), and locally

excited melatonin (LE2) (Figure 4.14). The main contribution comes from H-2→L (62%) which corresponds to CT2+LE1. The results are similar for higher transitions, but charge transfer from promazine to melatonin (CT1) starts at $S_0 \rightarrow S_3$ transition. It may be concluded that promazine-melatonin system has a tendency for charge transfer in gas phase similar to promazine-serotonin system but in contrast to the promazine-dopamine system.

Table 4.16. Excited state properties predicted by quantum chemical model calculations for promazine-melatonin in gas phase.

PZ-MT	ΔE (eV)	λ (nm)	$\Delta\mu$ (D)	f	Character	Predominant Transitions	%
S1	4.415	280.85	0.0029	0.0003	CT2+LE1 LE1+LE2 CT2	H-2 → L H-2 → L+1 H-1 → L	62 16 19
S2	4.750	261.04	0.2879	0.0335	LE1+LE2 CT2+LE2 CT2+LE2 CT2 CT2+LE2 CT2+LE2	H-2 → L+1 H-1 → L+3 H-1 → L+4 H-1 → L+7 H → L+1 H → L+3 H → L+4	32 21 16 11 12 40 26
S3	4.760	260.50	0.5434	0.0634	- CT2 LE1+LE2 CT1+LE1+LE2 CT1 CT1+LE1+LE2 CT1+LE1+LE2 CT1+LE1+LE2	H-8 → L H-2 → L H-2 → L+1 H-2 → L+3 H-1 → L+1 H-1 → L+3 H → L+3 H → L+4	10 14 48 11 20 10 24 16
S4	4.883	253.91	0.4336	0.0519	LE1+CT2 LE1+CT2 LE1+CT2 CT2	H-8 → L+1 H-3 → L H-3 → L+1 H-2 → L+2 H-1 → L+2	15 22 11 56 21
S5	5.048	245.62	0.4763	0.0589	CT2 CT2+LE1+LE2 CT2+LE1+LE2 CT1+LE1+LE2C CT1+LE1+LE2	H-1 → L+1 H-1 → L+3 H-1 → L+4 H-2 → L+3 H-2 → L+4 H-2 → L+6 H-2 → L+7	15 44 27 26 20 12 17
S6	5.428	228.42	1.0953	0.1457	LE1+CT1 CT1+LE1+LE2	H-3 → L H-3 → L+5 H-2 → L+3	26 11 38

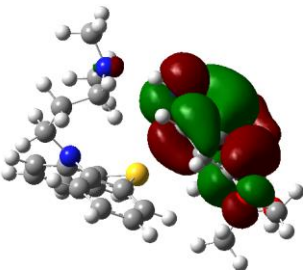
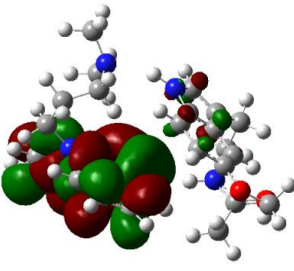
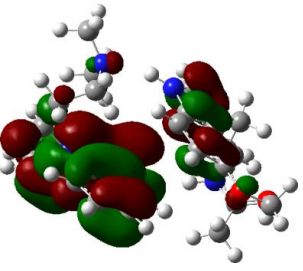
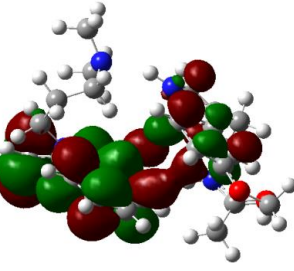
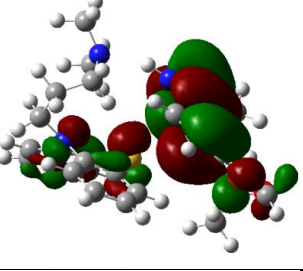
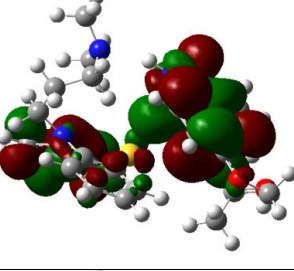
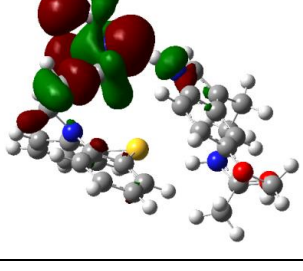
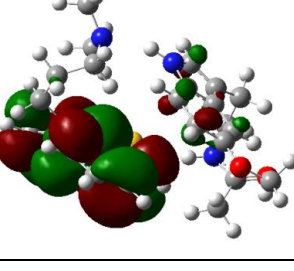
					CT1+LE1+LE2	H-2 → L+4	29
						H-2 → L+5	24
					CT2	H-1 → L	13
					CT2+LE2+LE1	H-1 → L+3	11
					CT2+LE2+LE1	H-1 → L+4	17

LE1: locally excited promazine

LE2: locally excited melatonin

CT1: charge transfer from promazine to melatonin

CT2: charge transfer from melatonin to promazine

	HOMO -6.86 eV		LUMO 1.36 eV
	H - 1 -7.05 eV		L + 1 1.47 eV
	H - 2 -7.29 eV		L + 2 1.71 eV
	H - 3 -8.27 eV		L + 3 1.90 eV

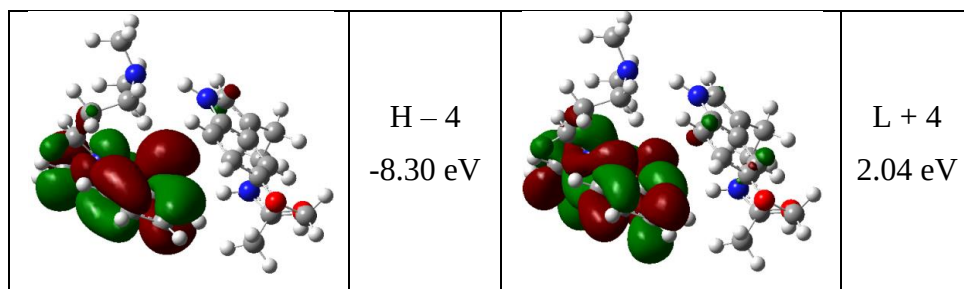


Figure 4.14. Molecular orbitals of promazine-melatonin system in gas phase involved in the CI-description of lowest excited singlet states

Table 4.17 and Figure 4.15 display the molecular orbitals and excited state properties of promazine-melatonin system calculated in water. In water, $S_0 \rightarrow S_1$ transition has only CT1 and CT2 characters. The main transition from H-1 $\rightarrow$ L corresponds to CT1 (64%) (Table 4.17). On the other hand, higher transitions are mixtures of CT1, CT2, LE1 and LE2. Results in water also support the conclusion that promazine-melatonin system has a tendency for charge transfer similar to promazine-serotonin system which is in contrast to the promazine-dopamine system.

Table 4.17. Excited state properties predicted by quantum chemical model calculations for promazine-melatonin system in water.

PZ-MT	ΔE (eV)	λ (nm)	$\Delta\mu$ (D)	f	Character	Predominant Transitions	%
S1	4.379	283.16	0.0096	0.0010	CT1	H-2 $\rightarrow$ L	20
					CT1	H-1 $\rightarrow$ L	64
					CT2	H-1 $\rightarrow$ L+2	10
S2	4.738	261.72	0.2518	0.0292		H-7 $\rightarrow$ L	12
						H-6 $\rightarrow$ L+3	11
						H-4 $\rightarrow$ L+4	13
					CT1+LE1	H-2 $\rightarrow$ L+1	22
					CT1	H-1 $\rightarrow$ L+1	52
					LE1+LE2	H-1 $\rightarrow$ L+2	24
S3	4.752	260.92	0.7409	0.0863	CT1	H $\rightarrow$ L+2	18
					CT2		
					CT2+LE2	H-2 $\rightarrow$ L+2	29
						H-2 $\rightarrow$ L+7	11
					LE1+LE2	H-1 $\rightarrow$ L+1	26
					CT2	H $\rightarrow$ L	13
S4	4.866	254.83	0.7628	0.0909	CT2+LE2	H $\rightarrow$ L+1	23
					CT2+LE2	H $\rightarrow$ L+2	44
					CT2+LE2	H $\rightarrow$ L+7	10
S4	4.866	254.83	0.7628	0.0909		H -7 $\rightarrow$ L	12

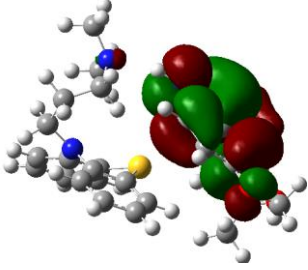
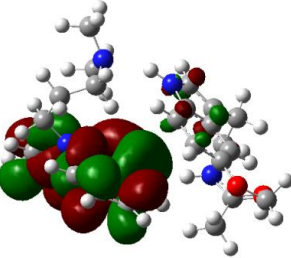
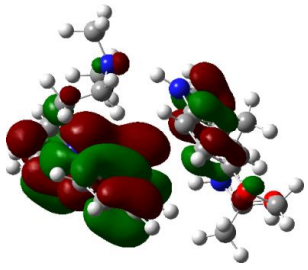
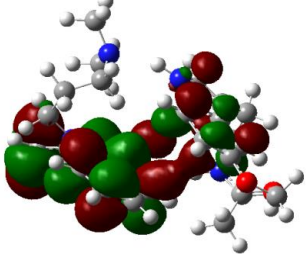
					LE1+CT1	H-6 $\rightarrow$ L+1	16
					CT2+LE2	H-4 $\rightarrow$ L	23
					CT1+LE1	H-2 $\rightarrow$ L+3	17
					LE1+CT2	H-1 $\rightarrow$ L+2	13
						H-1 $\rightarrow$ L+3	57
S5	4.993	248.35	0.7907	0.0967	CT2+LE1	H-2 $\rightarrow$ L	13
					LE1+CT2	H-2 $\rightarrow$ L+1	23
					LE1+LE2	H-2 $\rightarrow$ L+2	42
					CT1+LE1	H-1 $\rightarrow$ L+2	17
					CT2+LE2	H $\rightarrow$ L+1	16
					LE2+CT2	H $\rightarrow$ L+2	32
						H $\rightarrow$ L+7	17
S6	5.401	229.57	1.7002	0.2250	LE1+CT1	H-4 $\rightarrow$ L	33
					CT1+LE1	H-4 $\rightarrow$ L+1	12
						H-4 $\rightarrow$ L+6	14
						H-2 $\rightarrow$ L+6	10
					CT2	H-1 $\rightarrow$ L+3	20
					CT2	H-1 $\rightarrow$ L+4	33
						H-1 $\rightarrow$ L+5	14
						H-1 $\rightarrow$ L+6	26

LE1: locally excited promazine

LE2: locally excited melatonin

CT1: charge transfer from promazine to melatonin

CT2: charge transfer from melatonin to promazine

	HOMO -7.13 eV		LUMO 1.36 eV
	H - 1 -7.21 eV		L + 1 1.47 eV

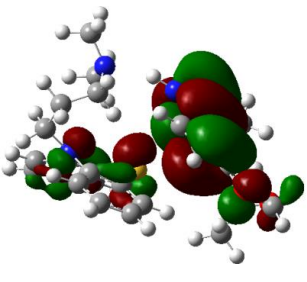
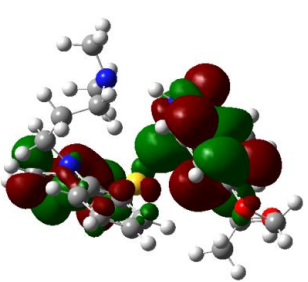
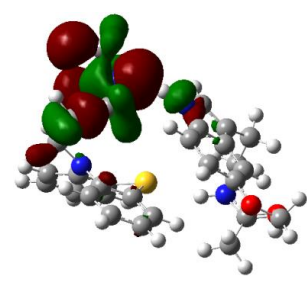
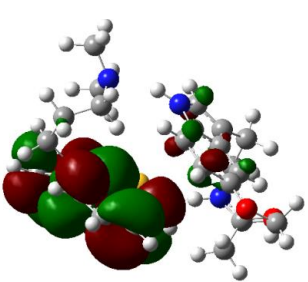
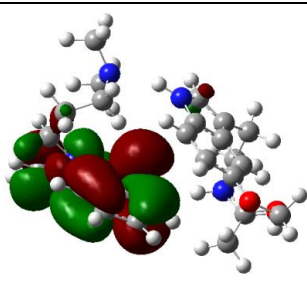
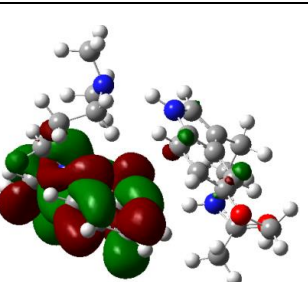
	H – 2 -7.35 eV		L + 2 1.66 eV
	H – 3 -8.14 eV		L + 3 1.71 eV
	H – 4 -8.24 eV		L + 4 2.01 eV

Figure 4.15. Molecular orbitals of promazine-melatonin system in water involved in the CI-description of lowest excited singlet states

4.2. Experimental Results

Absorption spectra of studied molecules were measured in water using Perkin Elmer Lambda 35 Spectrophotometer at room temperature. Results are given below in the order of monomers and dimers, respectively.

4.2.1 Promazine

Promazine has strong absorption intensity in water (Fig. 4.16). It shows two peaks in UV region at 302 and 252 nm. Promazine concentration was kept constant at 2.4×10^{-5} M in the study.

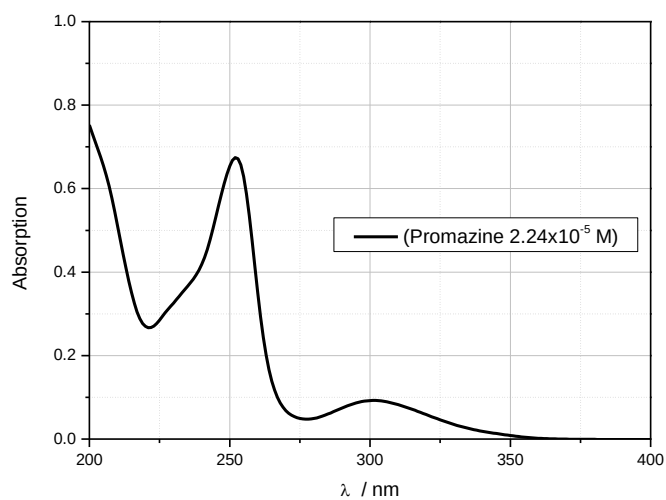


Figure 4.16. UV/Vis Absorption Spectrum of Promazine in water.

4.2.2 Dopamine

Dopamine has also strong absorption spectrum in UV region. Figure 4.17 shows absorption spectrum of Dopamine at 1×10^{-4} M in water. It has a peak at 280 nm.

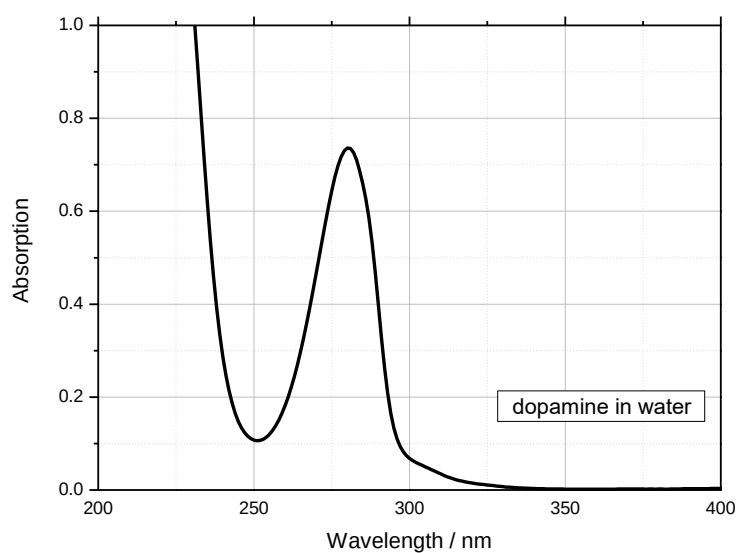


Figure 4.17. UV/Vis Absorption Spectrum of Dopamine in water.

Dopamine has strong fluorescence having maximum wavelength at 320 nm (Fig. 4.18, excitation wavelength 285 nm).

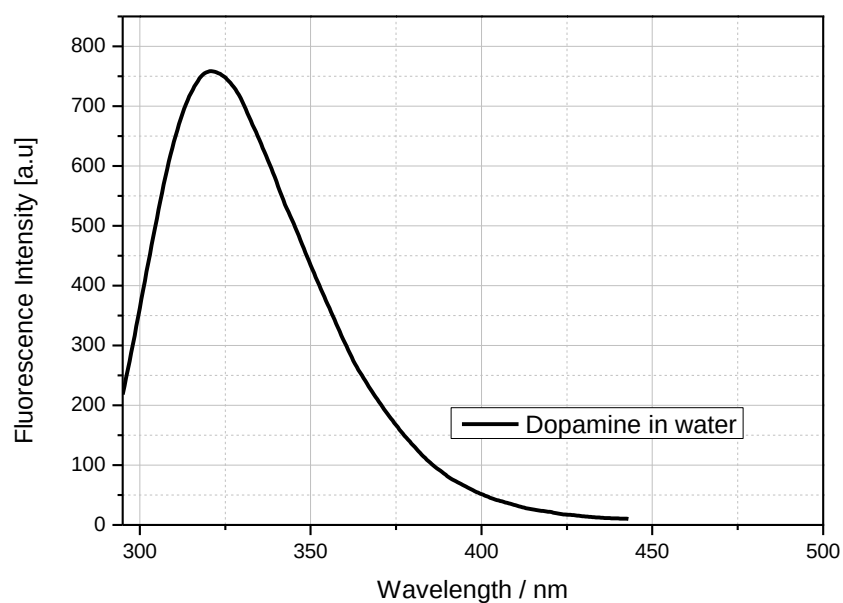


Figure 4.18. Fluorescence Spectrum of Dopamine in water.

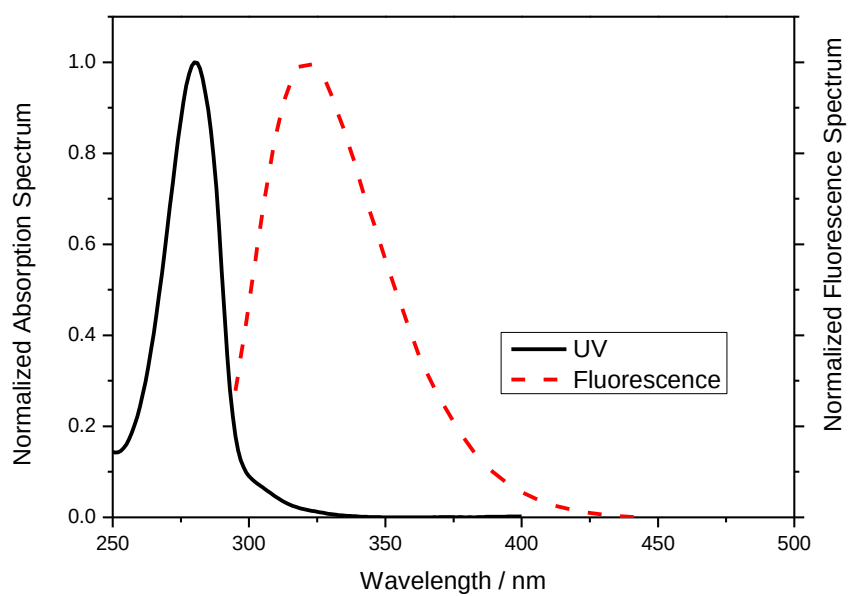


Figure 4.19 Normalized Absorption and Fluorescence Spectrum of Dopamine in water

Normalized Absorption and Fluorescence Spectra of Dopamine in water was shown in Fig. 4.19 Resonance wavelength was found from the spectra at $E_{00} = 294$ nm.

4.2.3 Serotonin

Serotonin displays a peak at 276 nm in water (Figure 4.20). Additionally, a shoulder is observed at 297 nm (Figure 4.20).

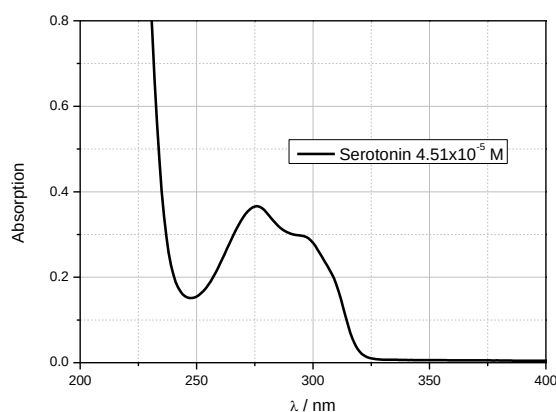


Figure 4.20 UV/Vis Absorption Spectrum of Serotonin in water.

4.2.4 Promazine-Dopamine

UV/Vis absorption spectrum (Figure 4.21) belonging mixture of promazine-dopamine in water is observed. In measurement, when concentration of dopamine (4.64×10^{-5} M) is fixed, concentration of promazine has been increased.

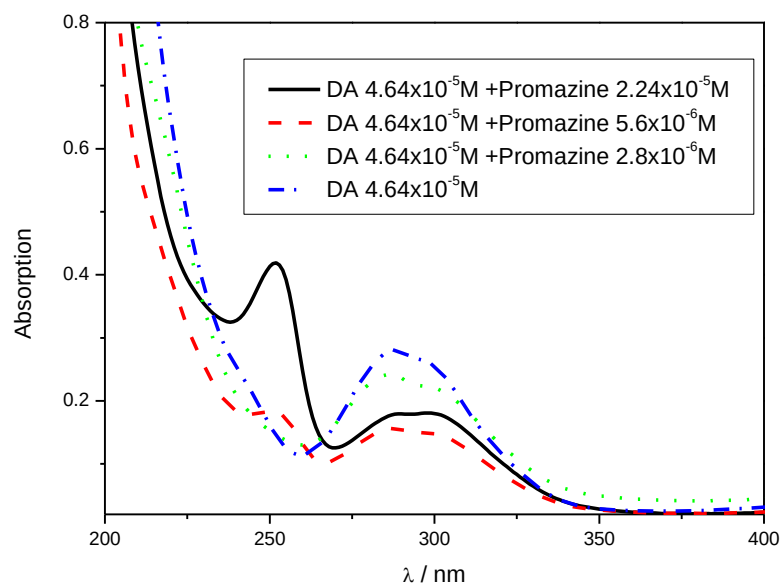


Figure 4.21 Absorption Spectra of Dopamine-Promazine System in water.

Different concentrations for the same system were examined in Figure 4.22. In both cases, dopamine and promazine characteristic spectra are protected. This shows that complex in basis state do not constitute.

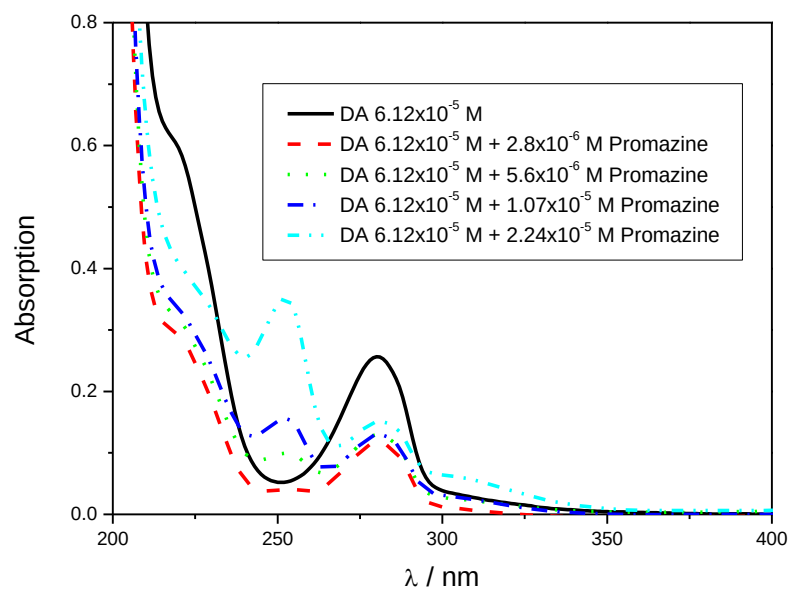


Figure 4.22 UV/Vis Absorption Spectra of Dopamine-Promazine System in water.

4.2.5 Promazine-Serotonin

UV/Vis absorption spectrum (Figure 4.23) belonging mixture of promazine-serotonin in water is observed. In measurement, when concentration of serotonin (4.51×10^{-5} M) is fixed, concentration of promazine has been increased. Shift was not observed the peaks due to complex in basis state did not occur.

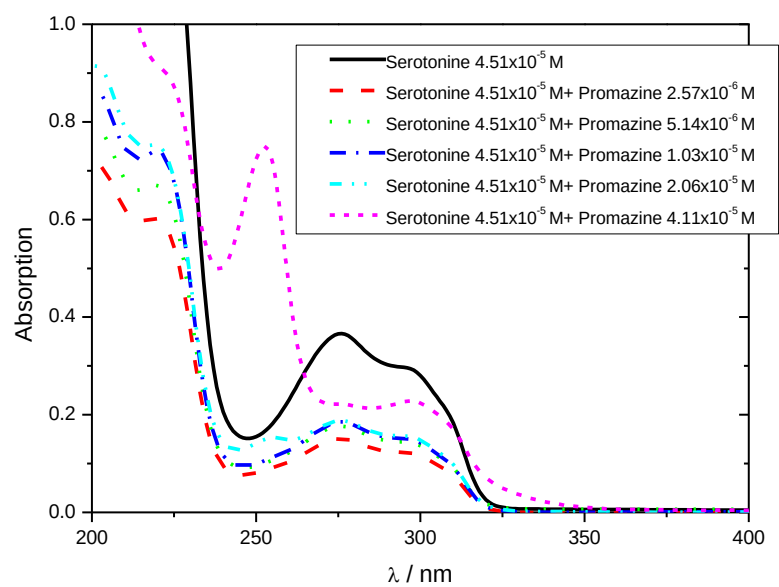


Figure 4.23 UV/Vis Absorption Spectra of Serotonin-Promazine System in water.

5. CONCLUSION AND FUTURE REMARKS

Both HOMO and LUMO are located mostly on the rings for all studied monomers. The results displayed for promazine and the hormones (Dopamine, Serotonin and Melatonin) indicate that there are no significant changes in the properties and molecular orbitals in gas phase and in water. Also, electron transition is easier in water than in gas phase. All complexes have different geometries in gas phase and in water. The first charge transfer from promazine to dopamine (CT1) is observed at $S_0 \rightarrow S_3$ from H-4 and H-3 to LUMO. It is clearly seen that charge transfer increases significantly at higher transitions in gas phase. In contrast to gas phase, the $S_0 \rightarrow S_1$ transition corresponds to charge transfer from dopamine to promazine (CT2) accompanied by a locally excited promazine (LE1). In all other transitions except $S_0 \rightarrow S_3$ charge transfer is the main process, but $S_0 \rightarrow S_3$ transition has been mostly dominated by locally excited promazine (LE1) and dopamine (LE2). The $S_0 \rightarrow S_1$ transition is a mixture of charge transfer from promazine to serotonin (CT1), charge transfer from serotonin to promazine (CT2), locally excited promazine (LE1), and locally excited serotonin (LE2). It may be concluded that promazine-serotonin system has a tendency for charge transfer in gas phase in water in contrast to the promazine-dopamine system. The $S_0 \rightarrow S_1$ transition is a mixture of charge transfer from melatonin to promazine (CT2), locally excited promazine (LE1), and locally excited melatonin (LE2) in gas phase. The main contribution comes from H-2 $\rightarrow$ L (62%) which corresponds to CT2+LE1. The results are similar for higher transitions, but charge transfer from promazine to melatonin (CT1) starts at $S_0 \rightarrow S_3$ transition. It may be concluded that promazine-melatonin system has a tendency for charge transfer in gas phase similar to promazine-serotonin system but in contrast to the promazine-dopamine system. In water, $S_0 \rightarrow S_1$ transition has only CT1 and CT2 characters. The main transition from H-1 $\rightarrow$ L corresponds to CT1 (64%). Experimentally, Dopamine and promazine characteristic spectra are protected. This shows that complex in ground state do not constitute.

Table 5.1. Main electronic transitions and corresponding wavelengths for the studied compounds and their complexes.

Molecules						
	in gas phase		in water		in water	
	transition	λ (nm)	transition	λ (nm)	transition	λ (nm)
PZ	S0 $\rightarrow$ S1	283.13	S0 $\rightarrow$ S1	283.91		
DA	S0 $\rightarrow$ S1	239.68	S0 $\rightarrow$ S1	240.37		280.00
SE	S0 $\rightarrow$ S1	259.00	S0 $\rightarrow$ S1	260.45		
MT	S0 $\rightarrow$ S1	258.52	S0 $\rightarrow$ S1	258.98		
PZ-DA	S0 $\rightarrow$ S1	306.00	S0 $\rightarrow$ S1	286.19		
	S0 $\rightarrow$ S3		S0 $\rightarrow$ S3			
PZ-SE	S0 $\rightarrow$ S1	289.85	S0 $\rightarrow$ S1	295.26		
PZ-MT	S0 $\rightarrow$ S1	280.85	S0 $\rightarrow$ S1	283.16		

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