METHODS OF CALCULATIONS

Methodologies

1. Conformational Analysis

Conformational analysis is the study of the conformations of a molecule and their influence on its properties. The conformations of the molecule are traditionally defined as those arrangements of the atoms in space that can be interconverted by rotation about single bonds. The objective of conformational analysis is to identify the "preferred' conformations of a molecule and to compare to those conformations which are important for the molecular activity. This usually requires locating conformations that are minimum points on *the potential energy surface (PES)*. Energy minimization methods therefore play a crucial role in the conformational analysis.

The way the energy of the molecular system varies with small changes in its structure is specified by its "potential energy surface" (PES). A potential energy surface is a remarkable graphical representation of individual molecules, molecular complexes and conformational interconversions, subject to the Born-Oppenheimer (BO) approximation. The BO approximation assigns a potential energy value to any fixed nuclear geometry and thus defines a $E = E(x_1,x_2,\ldots,x_N)$ potential energy function. The $x_1,x_2,\ldots,x_N$ coordinates represent nuclear coordinates in a particular coordinate frame, e.g., Cartesian coordinates, internal coordinates such as bond lengths, bond angles and torsion angles (dihedral angles), or interatomic distances. For a system with N atoms the energy is thus a function of $3N$-6 internal coordinates. It is therefore impossible to visualize the entire energy surface except for some simple cases where the energy is a function of just one or two coordinates. For example, the van der Waals energy of two argon atoms (as might be modeled using Lennard-Jones potential function) depends just on one coordinate: the atomic distance. Sometimes we may wish to visualize only a part of the energy hyper surface. For example, let us suppose we take an extended conformation of pentane and rotate the two central carbon-carbon bonds so that the torsion angles vary from 0°-360°, calculating the energy of each structure generated as shown in Figure 12. The energy in this case is a function of just two variables and can be plotted as a contour diagram or as an isomeric plot.

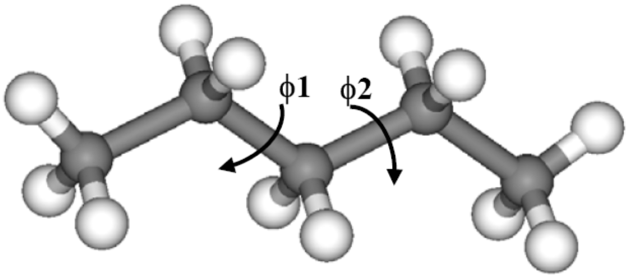


Figure 12 Variation in the energy of pentane with the two torsion angles indicted and represented as a contour diagram and isomeric plot.

The PES (see Figure 13) is a graphical representation of the potential energy function and allows an astonishingly simple link between key chemical concepts and basic geometrical features of the surface. In the context of conformational analysis, minima and saddle points on the PES are the most important features. Minima correspond to minimum energy conformations and saddle points correspond to transition states associated with conformational interconversion. A minimum energy conformation is defined by particular equilibrium atomic arrangement where, in the classical sense, any small movements of atoms lead increasing of energy. The corresponding PES representation, a local minimum, perfectly reflects this requirement because at a local minimum the gradient of the potential energy function, which represents the negative of the force acting upon the atoms, vanishes. Saddle points, just like passes in a mountain area, provide the easiest way to pass from one valley to another. On the PES, saddle points therefore represent transition states providing the lowest energy barriers of conformational interconversions. The above definition of a molecular conformation and conformational analysis all together assumes an ideal PES. In practice, however, the potential energy function behind the PES is subject to a number of approximations. In fact, there are a great many potential energy functions in use based on quantum mechanics (QM) or molecular mechanics (MM). MM potential termed force field are used almost exclusively for conformational analysis since QM potentials, although generally more accurate than MM potential, are impractical for large molecules.

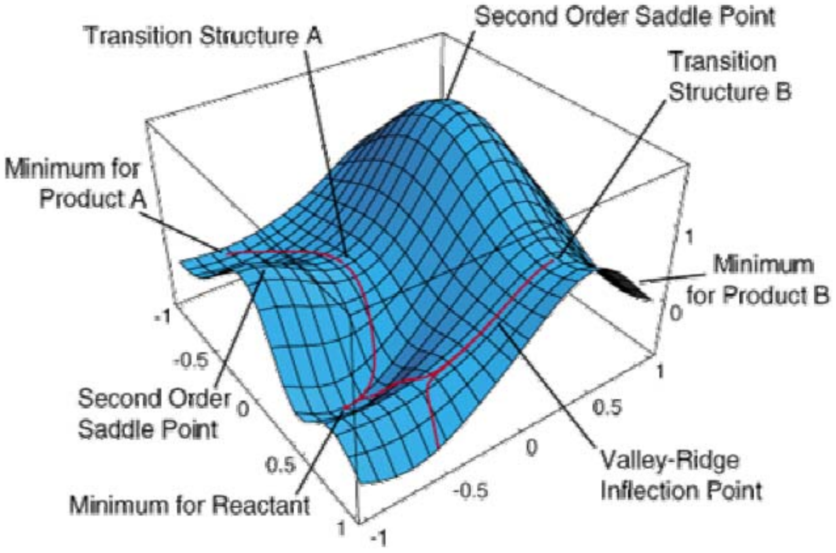


Figure 13 Potential energy surface (PES).

PES describes the energy of a system as a function of the nuclear coordinates defined as followed:

$$E(\vec{R}) = E_e(\vec{R}) + V_{nn}(\vec{R}) \qquad \text{with} \quad \vec{R} = (R_1, \ldots, R_{3M})$$

where E is the total energy of the system
E_e is the electronic energy
V_{nn} is inter-nuclear repulsion energy
R_A is Cartesian coordinate of nucleus A (mass M_A)
$\vec{R}$ is vector of $3M$ Cartesian coordinates of M nuclei.

From the classical motion of nuclei (molecular dynamics), the equation of motion can be written as:

$$M_A \frac{d^2}{d_t^2} R_A = F_A(\vec{R})$$

where F_A is the force on nucleus A as gradient of the total energy with respect to the permanent nuclear coordinates.

$$\vec{F} = (F_1,...,F_{3M})$$

with $F_i = -\nabla_{R_r} E(\vec{R})$; F_i is the component of the forces on the nuclei.

$$; \nabla_i = \frac{\partial}{\partial x_i} + \frac{\partial}{\partial y_i} + \frac{\partial}{\partial z_i}$$

As described above the PES corresponds to the local minima and saddle point where the first derivative of energy, know as the gradient or forces, are zero.

$$F_i = -\nabla_{R_r} E(\vec{R}) = 0$$

Since the gradient is the negative of forces, the forces are also zero for such a point. A point on the PES where the forces are zero is called a *stationary point*. This is the necessary condition for a local minimum but not sufficient condition for a local minimum. Therefore, the second derivative of the energy with respect to the molecular coordinates is then necessary to justify the characteristic of the stationary point. The second derivatives of energy or the first derivatives of the gradients with respect to the nuclear coordinates are defined as the *Hessian Matrix.*

$$\mathrm{H} = \begin{pmatrix} H_{11} & H_{1,3M} \\ H_{3M,1} & H_{3M,3M} \end{pmatrix}$$

$$\text{with} \quad H_{ij} = -\nabla_{R_i} F_j(\vec{R}) = \frac{d^2}{dR_i dR_j} E(\vec{R})$$

where H_{ij} stands for the force constants at the equilibrium configuration of the nuclei. The eigenvalues of Hessian Matrix define the local curvature at the stationary point. The local minimum can be defined when all eigenvalues are positive represented the curvature in all directions positive. It is the saddle point (of first order) when exactly one eigenvalue is negative representing the curvature to be negative in one direction but positive in all other directions.

If possible, it is desirable to identify all minimum energy conformations on the PES. However, the number of minima may be so large that it is impractical to contemplate finding them all. Under such circumstance it is usual to try and find all the accessible minima. The relative populations of molecules's conformations can be calculated using statistical mechanics via the Boltzmann distributions, though it is important to remember that the statistical weights involve contributions from all the degrees of freedom, including the vibration as well as the energies. The distribution among the conformers (or, for that matter, among conformations other than minimum energy ones) is governed by the Boltzmann function,

$$K = \exp(-\Delta G/RT)$$

where K is the ratio of mole fractions of the two conformations and ΔG is their free energy difference.

2. Spectroscopy, Photophysics and Photochemistry

If a substance is irradiated with electromagnetic radiation, the energy of the incident photons may be transferred to the atoms or molecules raising them from the ground state to an excited state. This process, known as *absorption*, is accompanied by attenuation of the incident radiation at a particular frequency and can occur only when the energy difference between the two levels is exactly matched by the energy of the photons. The frequency of the radiation is given by

$$E_2 - E_1 = \Delta E = h\nu \qquad (1)$$

where E_1 and E_2 are the energies of the two levels and ΔE is the difference between them. The absorbed energy is rapidly lost to the surrounding by collisions allowing the system to revert or relax to the ground state. Sometimes the energy is not dissipated in this way but is re-emitted a few million seconds later-a process known as *fluorescence*.

A useful way of representing the energies of the electronic states of molecule is a **Jablonski diagram**, such as in Figure 14. The vertical scale represents potential energy. The horizontal scale has no particular significance; it allows us to separate to singlet and triplet state **manifolds** (sets of energy levels) so that the excited states are more clearly distinguished. Superimposed on each electronic state is a set of vibrational energy levels. For the sake of clarity, a set of rotational energy levels superimposed on each vibrational level is not shown.

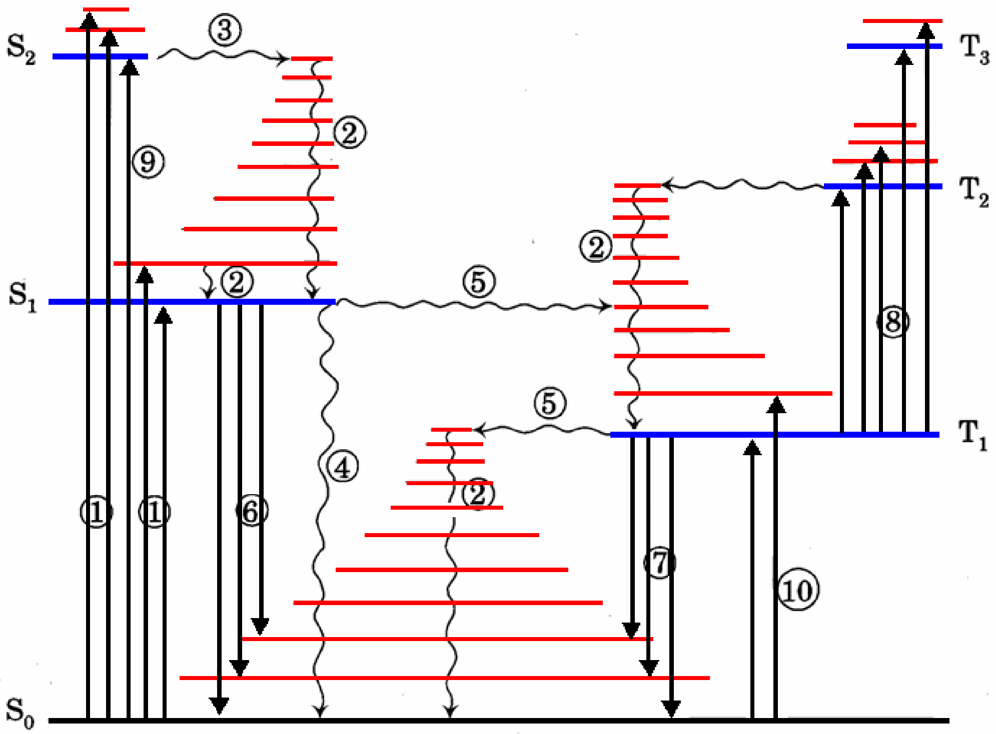


Figure 14 Generalized Jablonski diagram.

There are two kinds of photophysical processes indicated in Figure 14. Those interconversions denoted by straight lines are **radiative processes,** which occur through the absorption or emission of light. Those indicated by wavy lines are

nonradiative processes, which occur without light being absorbed or emitted. The numbers on the lines are keys to the following definitions:

1. **Absorption of Light**. A ground state molecule (S_0) may absorb a photon of light, thus becoming converted to an excited state. The most likely transitions are $S_0 \rightarrow S_1$ or $S_0 \rightarrow S_2$, although S_0 to higher excited singlet state transitions are also possible.

2. **Vibrational Relaxation.** The absorption from S_0 to S_n involves an energy change from the 0th vibrational level of S_0 to any vibrational level of the excited state. However, the $\nu^{//} = 0$ is also the vibrational level is the level most populated at room temperature for the ground electronic state of molecule, and $\nu^{/} = 0$ is also the vibrational level of the excited electronic state that is most likely to be populated at equilibrium. Unless the molecule dissociates before equilibrium can be obtained, there is a very rapid process (with a rate constant of about 10^{12} sec^{-1}) that relaxed the higher vibrational level of the excited state to its 0th vibrational level in condensed phases (i.e., solids or liquids).

3. **Internal Conversion** is a non radiative process that converts a higher electronic state into a lower state of the same multiplicity (a higher singlet state into a lower singlet state or a higher triplet state into a lower triplet state). The name arises because the process occurs internally, the line for internal conversion is a horizontal one. This means that the the 0th vibrational level of S_2 is converted into a vibrationally excited S_1 can then relax to its 0th vibrational level. The rate constants for internal conversion are fast ($> 10^{10}$ sec^{-1}), especially when the two states are close in energy.

4. **Radiationless Decay** is a process by which electronically excited states are returned to ground states (typically from S_1 to S_0) without the emission of light. Radiationless decay often has a slower rate constant (ca. $<10^{6}$ sec^{-1}) than other forms of internal conversion because the energy gap between S_1 and S_0 is usually greater than that between S_2 and S_1 or other pairs of excited states.

5. Intersystem Crossing, the conversion of a singlet state into a triplet state (or vice versa), requires a spin flip of an electron. The probability of intersystem crossing depends, among other things, on the energy gap between the singlet and triplet states, so values of k_{isc} vary from 10^6 to 10^{10} sec^{-1}. The T_n states is lower in energy than the corresponding S_n state because of the lower electron repulsion for unpaired electrons.

Processes 2-5 are nonradiative processes. The following are radiative processes.

6. Fluorescence is the emission of light from an excited state to a ground state with the same multiplicity. Usually the emission is $S_1 \rightarrow S_0$, and generalization to that effect is known as Kasha's rule. However, **anomalous fluorescence** ($S_2 \rightarrow S_0$) occurs in some compound, among them azulene, thiocarbonyl compounds, and some gaseous polyenes.

7. Phosphorescence is the emission of light from an excited state to a ground state with different multiplicity (usually from a triplet excited state to singlet ground state). This process involves both an electronic state change and a spin flip so, like $S_0 \rightarrow T_n$ absorption, phosphorescence is a spin-forbidden process.

8. Triplet-Triplet Absorption. A molecule in a triplet excited state may absorb a photon to give a higher triplet state, so a UV-Vis spectrum may be obtained, and the time-dependence of the excited state decay may be monitored. Flash spectroscopy is triplet-triplet absorption spectroscopy that can be an important technique for detecting triplet excited states.

9. Singlet-Singlet Absorption. Because triple states may persist longer than singlet states, the only excitation of excited states possible during much of the development of photochemistry was triplet-triplet absorption. With the advent of picosecond and femtosecond spectroscopy, it has become possible also to measure transitions from one excited singlet state to another, higher energy excited singlet state.

10. Singlet-Triplet Absorption, like phosphorescence, is a spin-forbidden process, so ordinarily $S_0 \rightarrow T_n$ transitions are not observed in UV-Vis spectroscopy. However, these transitions can be seen under certain conditions

For ultraviolet and visible wavelengths, one should expect that the absorption spectrum of a molecule (i.e., a plot of its degree of absorption against the wavelength of the incident radiation) should show a few very sharp lines. Each line should occur at a wavelength where the energy of an incident photon exactly matches the energy required to excite an electronic transition as shown in Figure 15.

In practice it is found that the ultraviolet and visible spectrum of most molecules consists of a few humps rather than sharp lines. These humps show that the molecule is absorbing radiation over a band of wavelengths. One reason for this band, rather than line absorption is that an electronic level transition is usually accompanied by a simultaneous change between the more numerous vibrational levels. Thus, a photon with a little too much or too little energy to be accepted by the molecule for a 'pure' electronic transition can be utilize for a transition between one of the vibrational levels associated with the lower electronic state to one of the vibrational levels of a higher electronic state.

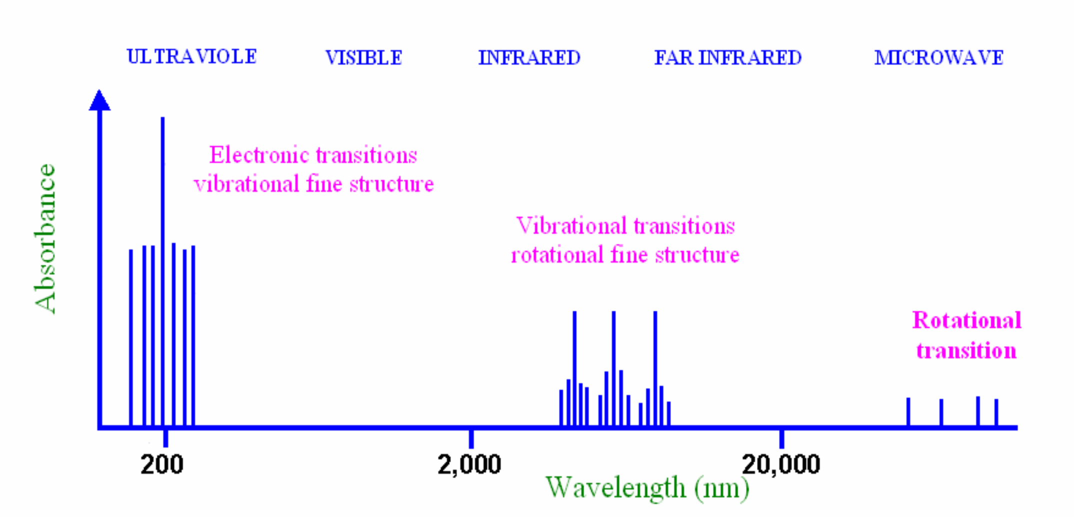


Figure 15 Idealized absorption spectrum.

If the difference in electronic energy is ‘E’ and the difference in vibrational energy is ‘e’, then photons with energies of E, E+e, E+2e, E-e, E-2e, etc. will be absorbed.

Furthermore, each of the many vibrational levels associated with the electronic states also has a large number of rotational levels associated with it. Thus a transition can consist of a large electronic component, a smaller vibrational element and an even smaller rotational change. The rotational contribution to the transition has the effect of filling in the gaps in the vibrational fine structure. In addition, when molecule are closely packed together as they normally are in solution, they exert influences on each other which slightly disturb the already numerous, and almost infinite energy levels and blur the sharp spectral lines into bands.

Fluorescence and Phosphorescence

For most organic molecules, fluorescence is the spontaneous emission of light from the $\nu^{/} = 0$ vibrational level of the first excited singlet state to some vibrational level ($\nu^{//} = 0, 1, 2, \ldots$) of the (singlet) ground electronic state. As indicated in the top portion of Figure 16, the energy of the photon emitted in the $\nu^{/} = 0$ to $\nu^{//} = 0$ fluorescence is the same as the energy of the photon absorbed in the $\nu^{//} = 0$ to $\nu^{/} = 0$ transition if the geometry of the photoexcited molecule is nearly the same as that of the ground state molecule. However, all other fluorescence lines are at longer wavelengths (lower energy). Thus, the fluorescence and emission spectra should overlap at the 0,0 transition, providing confirmation of the 0,0 energy of the electronically excited state. In molecules such as anthracene, the σ bonding provides a molecular framework for the planar π system, and the π bonding results from population of many bonding MOs. Therefore promotion of one electron to an antibonding MO may not seriously distort the molecular geometry. In such cases there can be a nearly mirror image relationship between the absorption and fluorescence spectra of organic molecules, particularly when the spectra are plotted as intensity versus energy (cm^{-1}) instead of wavelength. The similarity arises because the factors that make some $\nu^{//} = 0$ to $\nu^{/} = x$ transitions more probable than others also make some $\nu^{/} = 0$ to $\nu^{//} = x$ emissions more probable.

For some molecules, however, the geometry of the ground and excited states may be very different. As a result, there may be a large difference between λ_{max} for absorption and λ_{max} for emission, and the 0,0 transition may be weak or not present.

A similar relationship between geometry and a mirror image appearance of singlet-triplet absorption and phosphorescence is expected, but this is often difficult to determine experimentally, In fluid solution phosphorescence is usually reduced by diffusion-limited bimolecular interaction of the excited triplet compound and one or more ground state species. However, phosphorescence can often be observed by irradiating the compound in environments in which diffusion is quite slow, such as in an organic glass at liquid nitrogen temperature.

Singlet-triplet absorption is ordinary difficult to detect because the transition is spin-forbidden. Heavy atom solvents or oxygen perturbation have been used to induce singlet-triplet absorption, but absorptions observed in this manner are weak, and it is important to establish that the observed absorption is not due to artifacts resulting from the solvent or additive.

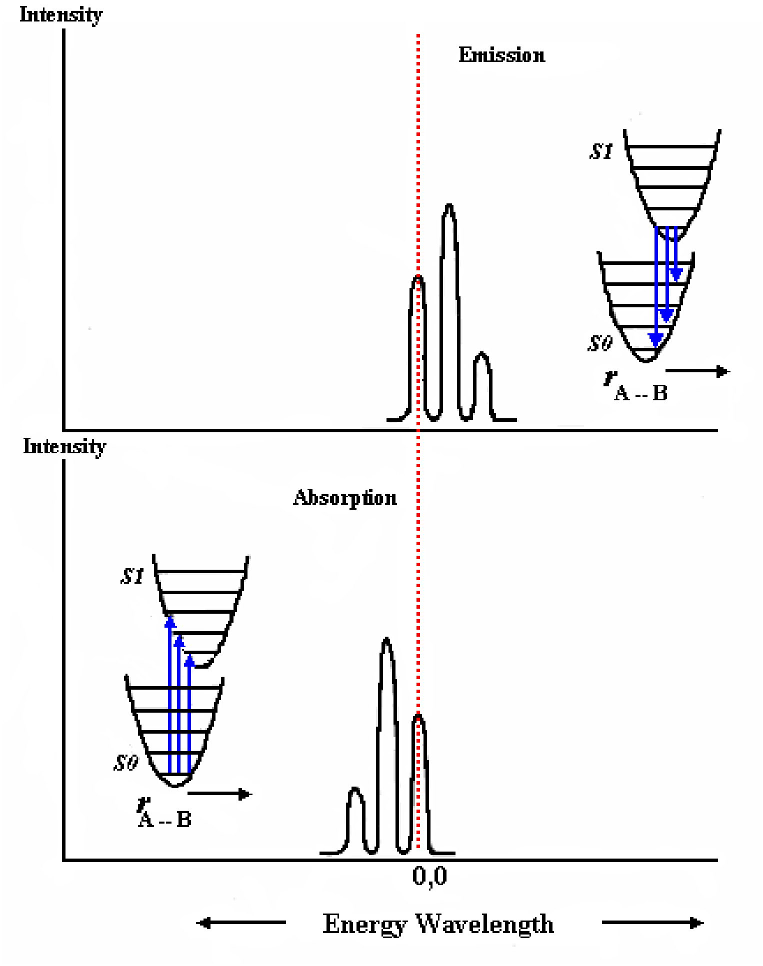


Figure 16 Schematic representations of the origins of UV-Vis absorption (bottom) and fluorescence (top) spectra.

Franck-Condon principle

The different electronic states of a molecule are often associated with different shapes of molecule because the different electron distribution around the molecule changes the electrostatic Coulombic forces that maintain the nuclei in specific relative positions. Since nuclei are considerably more massive than electrons, the Franck-Condon principle states that:

an electronic transition takes place sufficiently rapidly that the nuclei do not change their internuclear positions during the transition.

Consequently, when energy is absorbed in an electronic transition, the nuclei suddenly find themselves in a new force field and at positions which are not in equilibrium for the new electronic state. This is shown schematically in Figure 17, in which an electronic absorption from the ground state appears as a vertical line because of the Franck-Condon principle. The internuclear separation of the ground state becomes a **turning point,** the extent of maximum displacement, in a vibration of the excited state.

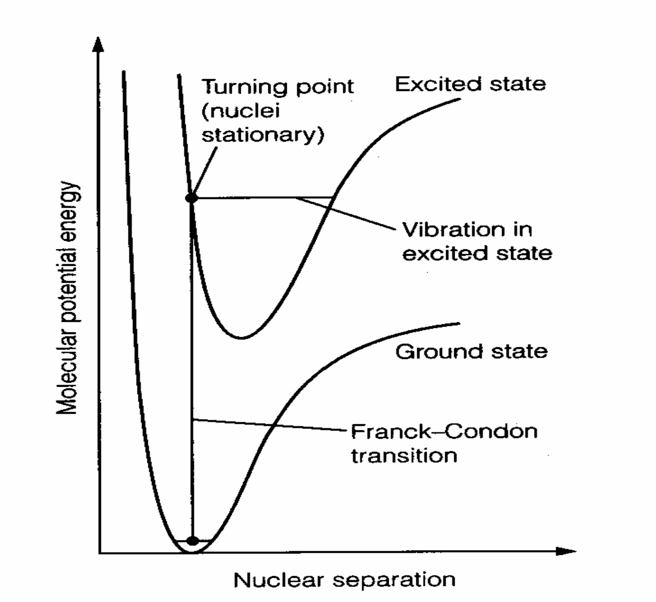


Figure 17 Illustration of the Franck-Condon principle for vertical electronic transitions.

The vertical transition has the greatest transition probability but transitions to nearby vibrational levels also occur with lower intensity. Therefore, instead of an electronic absorption occurring at a single, sharp line, electronic absorption consists of many lines each corresponding to the stimulation of different vibrations in the upper state. This vibrational structure (or progression) of an electronic transition can be solved for small molecules in the gas-phase, but in a liquid or solid collision broadening of the transitions cause the lines to merge together and the electronic absorption spectrum is often a broad band with limited structure (Figure 18). The Franck-Condon principle also applies to downward transitions and accounts for the vibrational structure of a fluorescence spectrum.

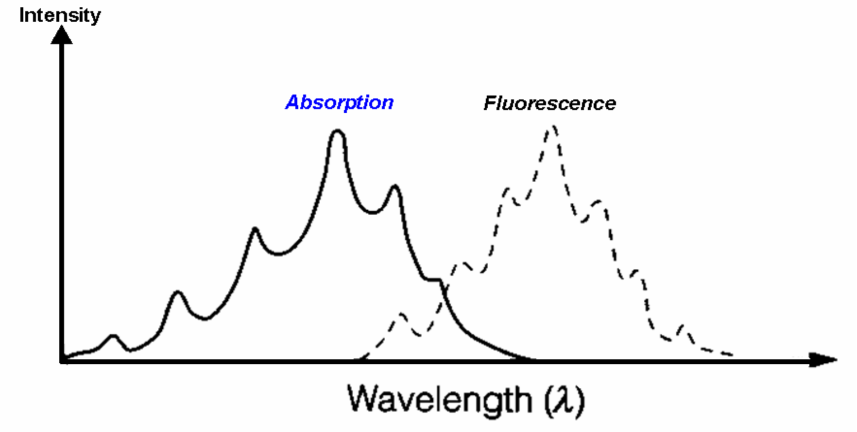


Figure 18 Relationship between the broad electronic absorption and fluorescence bands of liquids and solid

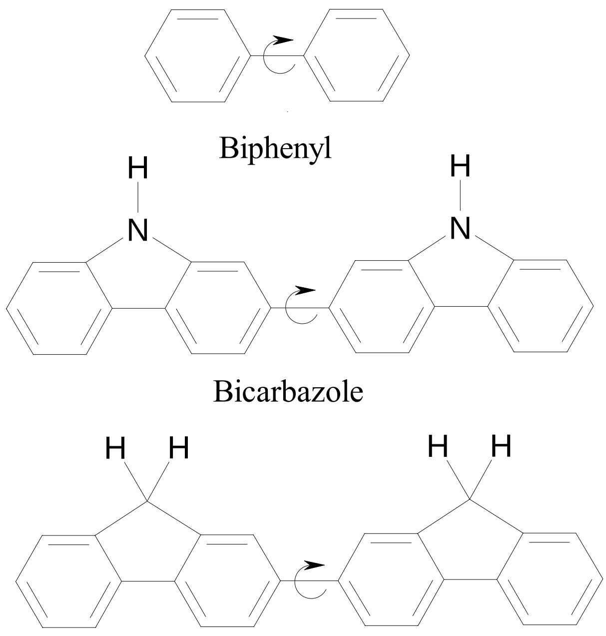
Computational Details of Calculations

1. The Torsional Potential for Bicarbazole and Bifluorene at High-Level *ab initio* and DFT Results

The aim of this work to investigate the potential energy surface for the bicarbazole and bifluorene, using distinct theoretical approaches and basis sets, aiming to assess the role played by both correlation effects and the size of the basis set for the determination of the equilibrium and transition state structures located on the torsional potential energy. In addition to, this procedure has tested by several methods to study the potential energy surface of biphenyl molecule and we showed that this process can be used to validate methods for conformational analysis. The following basis sets were used: Pople's and Dunning's basis sets have been chosen.

1.1 Conformational Analysis

The starting geometries of the oligomers were constructed by SciPolymer 3.0 program (SciVision 3.0). The torsional potential energy for biphenyl, bicarbazole and bifluorene (Figure 19) were investigated using quantum chemical methods at the HF, MP2 method and several DFT functional. The hybrid BH&HLYP and B3LYP were used. The following basis sets were used Pople's basis sets, 6-31G(d), 6-311G(d,p), 6-311++G(2d,2p) and Dunning's double-zeta (cc-pVDZ, cc-pVTZ, aug-cc-pVDZ and aug-cc-pVTZ). For consistency, the 6-31G, 6-31G(d), 6-311G(d,p), 6-311++G(2d,2p) cc-pVDZ and cc-pVTZ basis set has been chosen for all molecules at HF and DFT levels of description considered. As far as the computational resources allowed that, a few larger basis sets were applied as well, however, not for all molecules and methods. The cc-pVDZ basis was used for MP2 calculations on all molecules. All stationary points located on the torsional energy were characterized as minima by harmonic frequency calculations (for minimum energy structures all frequencies are real).



Biphenyl

Bicarbazole

Bifluorene

Figure 19 Molecules discussed in this work, biphenyl, bicarbazole and bifluorene.

The relative energies of the rotamers were fitted to a six-term truncated Fourier expansion, as shown below, where *V* is the relative energy at torsional angle ø. Fully relaxed single-bond torsional potentials were calculated; i.e., for each fixed torsional angle around the central single-bond (ranging from 0° to 180°, in increments of 30°), all remaining internal degrees of freedom were optimized for each of the methods and each of the basis sets chosen. A rather tight, regular 10^{o} of points was applied in most cases. For some of the more expensive, larger basis set MP2 calculations a wider 30^{o} was calculated only. The energies thus obtained were subsequently least-squares-fitted to a simple analytical form, which has been used by most workers in the field:

$$V(\phi) = \sum_{n=1}^{m} \tfrac{1}{2} V_n (1 - \cos n\phi), \qquad (1)$$

with *m* varying from 4 to 8 in order to check the convergence of this series. In the case of bicarbazole and bifluorene ø is defined as 180-θ, where θ is the torsional angle and θ = 0 corresponds to the syn or s-cis structure. For the remaining biphenyl molecules, the potential is symmetric around ø = 90^o.

1.2 The Vertical Excitation Energy

Above procedure has been tested methods for study the potential energy of bicarbazole and bifluorene molecule and we showed that, which methods can be used to obtain good optimized geometries of the ground state. The vertical excitation energies were calculated within the framework of TD-DFT at the B3LYP with the 6-311++G(2d,2p) basis set. TD-(B3LYP/6-311++G(2d,2p)) were then performed by single point calculations at the optimized geometries of the ground state.

The vertical excitation energies were calculated within the framework of TD-DFT. Traditional *xc*-potentials such as the basic local density approximation (LDA) and the generalized gradient approximation (GGA) due to Becke and Perdew (BP86) and Hybrid Methods with correct asymptotic behavior were employed. TD-DFT at the BLYP, BP86, BH&HLYP, PBE1PBE and B3LYP levels, with the 6-311++G(2d,2p) basis set, were then performed by single point calculations at the optimized geometries of the ground state. The ground state geometries of carbazole-based molecules were fully optimized using B3LYP/6-311G(d,p) calculations. For comparison, the SAC-CI calculations were performed for the excitation energy by using the double-zeta (D95) basis set of Huzinaga and Dunning. All quantum chemical calculations were performed with the Gaussian 03 suite of programs (Frisch *et al.*, 2004).

2. Theoretical Investigation of Structural and Electronic Properties of Conjugated Polymers Based on Fluorene, Carbazole, Dibenzofuran and Dibenzothiophene Oligomers

The aim of this chapter is to computed the equilibrium structures and excitation energies of fluorene $(FL)_N$, carbazole $(Cz)_N$, dibenzofuran $(DBZF)_N$ and dibenzothiophene $(DBZTh)_N$ (see Figure 20) oligomers were computed using the density functional theory (B3LYP and BH&HLYP).Four basis sets, 6-31G, 6-31G(d), 6-311G(d,p) and 6-311++G(2d,2p), were used for calculating the properties of monomers.

2.2 Starting geometry

The starting geometries of the oligomers were constructed by SciPolymer 3.0 program (SciVision 3.0). First of all, the ground-state geometries of monomers were fully optimized using the density functional theory (B3LYP and BH&HLYP) calculations, starting from structural data, regularized in order to satisfy the C_{2v} symmetry. ZINDO and TD-B3LYP/6-311++G(2d,2p) calculations of the excitation energies were then performed at the optimized geometries of the ground states. We have investigated the basis set dependence of excitation energies calculated with TD-B3LYP/6-311++G(2d,2p) for these monomers.

2.2 Conformational Analysis

Second, the potential energy surface of each dimer, $(FL)_2$, $(CZ)_2$, $(DBZF)_2$ and $(DBZTh)_2$, were investigated by partial optimization, based on the density functional theory method, at the B3LYP and BH&HLYP methods. The dihedral angle is defined as the angle between the planes formed by the two units of monomer. Symmetry restrictions were imposed during the optimization. Potential energy curves, relative energy vs torsional angle (ø), of each dimer were drawn. Structures at various torsional angle values (from ø = 0° to ø = 180° in steps of 10°) were partially optimized by density functional theory methods.

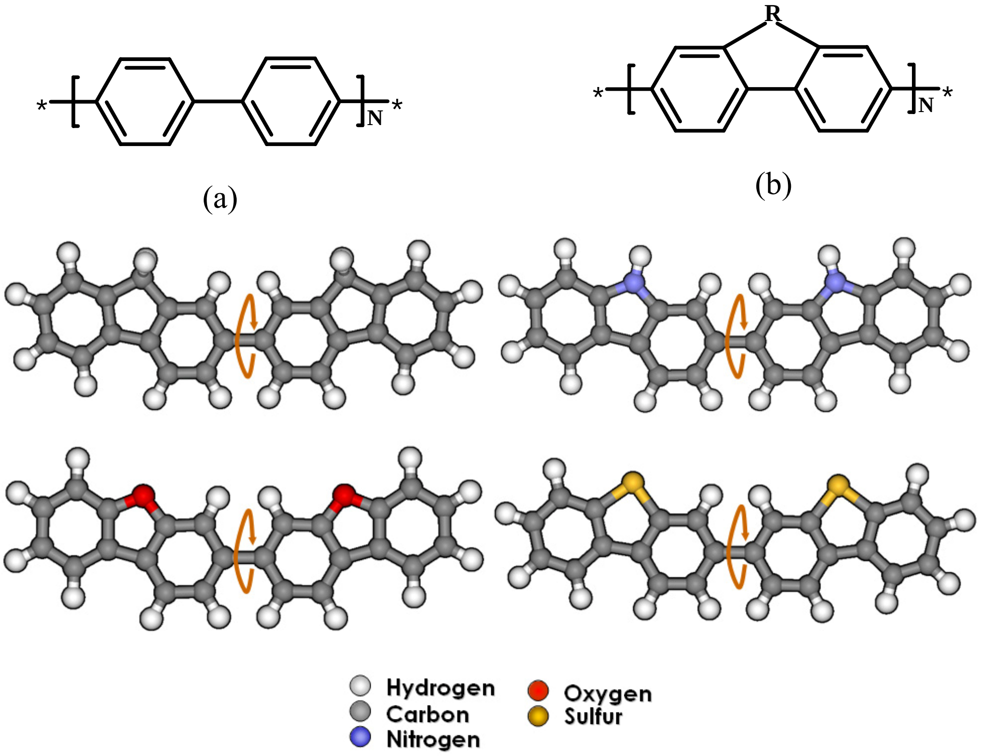


Figure 20 Schemetic structure of oligomers: (a) biphenyl and (b) oligomer of fluorene $(FL)_N$ (R= >CH_2), carbazole $(Cz)_N$ (R= >NH), dibenzofuran $(DBZF)_N$ (R= >O) and dibenzothiophene $(DBZTh)_N$ (R= >S).

2.3 HOMO-LUMO and Vertical Excitation Energy

Finally, the ground-state geometries of the oligomers (hereafter denoted by N=2 since it contains two repeating units), trimer (N=3), tetramer (N=4) of $(FL)_N$, $(CZ)_N$, $(DBZF)_N$ and $(DBZTh)_N$ were fully optimized using the B3LYP level of theory with the 6-311(d,p) basis set. The chains were set to be twist conformations. The calculations of the excitation energies were then performed based on the ground-state geometries. Excitation energies were calculated using the TD-B3LYP/6-311G(2d,2p) method and extrapolated to the polymer. The linearity between the calculated the energy of the oligomers and the reciprocal chain length is excellent for homologous series of oligomers.

3. Theoretical Investigation on Electronic Transition of Carbazole-Based Molecules by TD-DFT Methods

The aim of this chapter to study the torsional energy curves for the carbazole-based molecules (Figure 21) by using various theoretical approaches and basis sets. The effect of the size of the basis sets in determining the equilibrium and transition state structures with respect to the torsional energy was assessed. They were used here to describe the nature of the conformational analysis of five carbazole-based molecules: Cz-dimer, Cz-co-Phenyl (Cz-co-P), Cz-co-Fluorene (Cz-co-Fl), Cz-co-Thiophene (Cz-co-Th) and Cz-co-Furan (Cz-co-F). Also, the electronic properties of these molecules as calculated by TD-DFT, in combination with a variety of exchange-correlation functions and basis sets, were compared to the electronic structures and the excitation energies of the compounds.

3.1 Conformational Analysis of Carbazole-Based

The starting geometries of the oligomers were constructed by SciPolymer 3.0 program (SciVision 3.0). The torsional energy curves of each carbazole-based molecule, Cz-dimer, Cz-co-Phenyl (Cz-co-P), Cz-co-Fluorene (Cz-co-Fl), Cz-co-Thiophene (Cz-co-Th) and Cz-co-Furan (Cz-co-F), were investigated by partial optimization, based on the B3LYP method. Four basis sets, 6-31G, 6-31G(d), 6-311G(d,p) and 6-311++G(2d,2p), were utilized for this purpose.

The torsional angle (θ) is defined as the angle between the planes formed by the two heterocyclic carbazole-based units, and $\theta = 0°$ corresponds to the syn or cis structure. Structures at various torsional angles (from $\theta = 0°$ to $\theta = 180°$ in steps of 30°) were partially optimized.

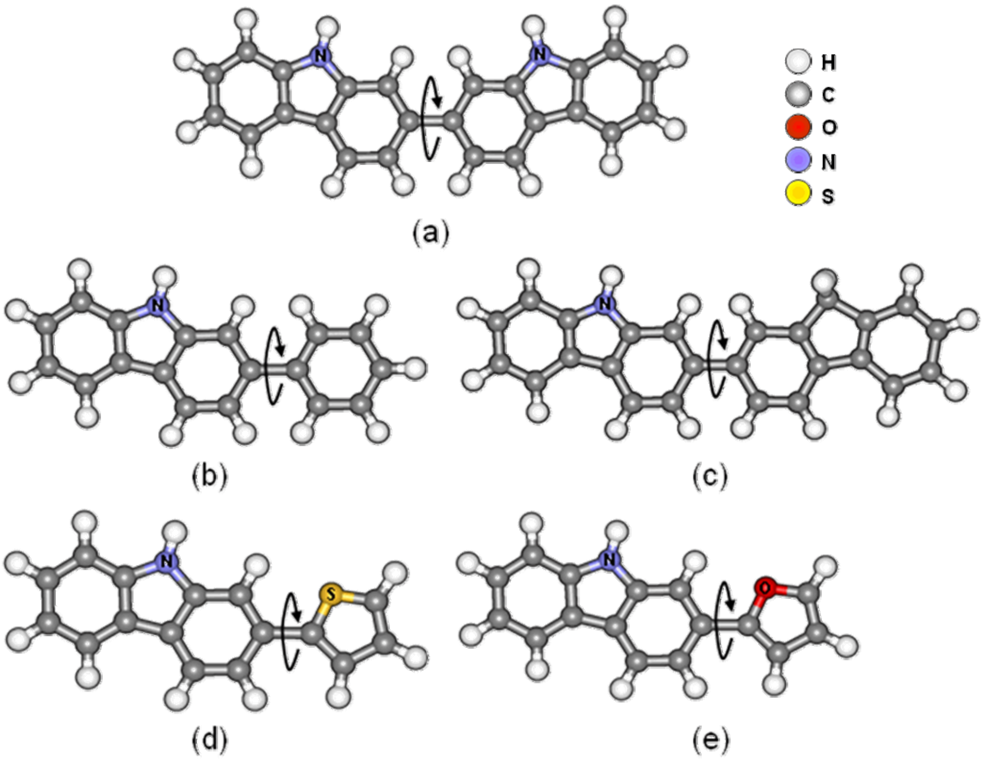


Figure 21 Chemical structures of carbazole-based molecules: carbazole combined with (a) Carbazole (Cz-dimer), (b) Phenyl (Cz-co-P), (c) Fluorene (Cz-co-Fl), (d) Thiophene (Cz-co-Th) and (e) Furan (Cz-co-F).

The relative energies of the rotamers were fitted to a six-term truncated Fourier expansion, as shown below, where *V* is the relative energy at the torsional angle θ.

$$V(\theta) = \sum_{n=1}^{m} \tfrac{1}{2} V_n (1 - \cos n\theta)$$

The energies thus obtained were subsequently least-squares-fitted to a simple analytical form. In general, *n* can be varied from 4 to 8 in order to check the convergence of this series.

3.2 Excitation Energy Calculations

The vertical excitation energies were calculated within the framework of TD-DFT. Traditional *xc*-potentials such as the basic local density approximation (LDA) and the generalized gradient approximation (GGA) due to Becke and Perdew (BP86) and Hybrid Methods with correct asymptotic behavior were employed. TD-DFT at the BLYP, BP86, BH&HLYP, PBE1PBE and B3LYP levels, with the 6-311++G(2d,2p) basis set, were then performed by single point calculations at the optimized geometries of the ground state. The ground state geometries of carbazole-based molecules were fully optimized using B3LYP/6-311G(d,p) calculations. For comparison, the SAC-CI calculations were performed for the excitation energy by using the double-zeta (D95) basis set of Huzinaga and Dunning. All calculations were performed by the Gaussian03 package (Frisch *et al.*, 2004), on an Intel Pentium IV 3.3 GHz PC running Linux.

4. Understanding on Absorption and Fluorescence Electronic Transitions of Carbazole-Based Conducting Polymers

The aim of this chapter to understand the structural geometries and electronic properties of ground state and excited stated of $(Cz)_2$, carbazole-co-fluorene (Cz-co-Fl) and carbazole-co-thiophene (Cz-co-Th) oligomers (Figure 21) by using the DFT and RI-CC2 method for the calculations.

4.1 Optimized Geometry of Oligomer

The starting geometries of the oligomers were constructed by SciPolymer 3.0 program (SciVision 3.0). The ground state and the lowest singlet excited-state geometries of the carbazole-based oligomers were optimized at the *ab initio* RI-CC2 at the DFT and TDDFT levels, respectively, using the B3LYP functional.

4.2 Electronic Properties Calculations

On the basis of the optimized geometries, the electronic absorption and luminescence spectra were calculated at the RI-CC2, DFT and TDDFT levels of theory. Vertical excitations are computed at the ground-state geometry by using RI-CC2 and DFT (B3LYP/SVP and B3LYP/TZVP). The polarized split-valence (SVP) and the triple-zeta valence-polarized (TZVP) basis sets have been used. The fluorescence transitions are obtained as the vertical de-excitation at the optimized geometry of by using TD-B3LYP/SVP method. All calculations were done using the TURBOMOLE version 5.7 program packages (Ahlrichs *et al.*, 1989).