Molecular interaction of 5cb and coronene molecules: A DFT study

Shiv Prasad Pandey, Alok Shukla*, A.K. Dwivedi
Department of Physics,
M. L. K. P. G. College Balrampur (U.P.) 271201 INDIA

Abstract

In the present investigation, we report the molecular interaction of 5cb and coronene molecules using the DFT method with the functional B3LYP with a basis set of 6-311G(d,p). All calculations are done in the Gaussian 09 programme. The optimised molecules' highest occupied molecular orbital (HOMO) and lowest vacant molecular orbital (LUMO) are plotted. Global parameters such as ionization potential (I), electron affinity (A), electronegativity (χ), global hardness (η), and softness (S) have been calculated in terms of energies of HOMOs and LUMOs using Koopman's theorem. Furthermore, the IR and Raman spectra of all molecules have been computed.

Keywords: Interaction energy, Liquid crystal, DFT, 5CB, Coronene, Spectroscopy

I.   Introduction

Computational chemistry deals with physical and chemical problems of molecular systems by computer stimulation [1-3] that cannot be solved analytically to complement the information provided with the experiment. It provides approximate solutions for system interaction with each other wherein affects interaction energies and the exchange of energies dominate. Researchers and Scientists need to study the nature of molecules in terms of their structures rather than examining them experimentally for each property. The wave function provides complete microscopic information of the system with a large number of particles under consideration. These systems are specified with Hamiltonian with nuclei at rest and electrons are in orbital motion relative to nuclei. Certain set of approximations necessitates the introduction of a new field of science covering aspects like condensed matter physics, quantum chemistry, atomic physics, and molecular physics. Approaches to fields of science are investigated with methods like (i) Mean-field theory, (ii) Hartree-Fock method, and (iii) density functional method. The wave function completely determines the system attributed to the Schrödinger equation and its solution. This equation provides information about the eigenvalues (energy) and eigenfunctions of systems. Generally for large numbers of systems, under consideration, solution of the Schrödinger equation is tedious and an attempt to provide a solution to these molecular systems that has its roots in the basic method (i) Ab-Initio, based on quantum mechanics and their physical constants, and (ii) Semi-empirical methods utilise additional empirical parameters. These methods involve the Born-Oppenheimer approximation providing a solution to the Schrödinger equation with the assumption that the total wave function is expressed as a product of the individual wave functions of the electron and nuclei. This approximation results from the change in the masses of the nuclei and electrons further with the difference in the electronic energies that arises due to the repulsive interaction between the electrons and nuclei and the attraction of the electron and nucleus. These methods attempt to determine the solution of Schrödinger equation with the position of nuclei, electron density, and energies of the system [4-8].

The density functional theory aims at determining the properties of systems as a function of the spatial dependence of the electron density, particularly in the ground state. Many electron systems have gained importance where electron correlation and exchange interactions prevail that are expressed as functions of functional. DFT aims at predicting the behaviour of materials with a construct of potential as a sum of the external potentials that arise due to the structure and composition of the material and the effective potential due to inter-electronic interactions [9-13].

Computational techniques with various methods enable to understand and design new molecular systems in relation structure with accuracy. The investigated parameters dependent on structure and geometry are bond lengths, bond angles, dipole moment, molecular energy, reaction rate, vibration studies, transition probabilities, and chemical reactivity.

II. Methodology

In the present paper, we use the DFT method with the B3LYP functional [13,14] with a basis set of 6–311G(d,p). All calculations are done using Gaussian 09 program [15]. The highest occupied molecular orbital (HOMO) and the lowest vacant molecular orbital (LUMO) of optimised LC molecules are plotted [16,17]. Global parameters such as ionization potential (I), electron affinity (A), electronegativity (χ), global hardness (η), and softness (S) have been calculated in terms of energies of HOMOs and LUMOs using Koopman's theorem [18–23]. Furthermore, the IR and Raman spectra of all molecules have been computed.

III. Results and Discussion

In this section, the study of the spectral and electronic properties of 5CB and coronene molecules has been carried out. Observations are reported in the following three subsections. In first subsection, we have discussed the optimized parameters of 5CB and coronene molecules and compared the obtained parameters. In second and third subsection, the frontier molecular orbital and electronic properties of the 5CB molecules with coronene have been studied.

3.1 Geometry optimisation

The optimized geometries of 5CB and coronene molecules are shown in Figure 1. The magnitude of the minimum energy of the 5CB molecule and the coronene molecule is -752.3082 and -922.0931 a u. The composite system of 5CB and coronene molecules has an energy of -1674.4032. Dipole moments of the 5CB, coronene, and composite system are 5.9842, 0.0, and 6.0733 Debye respectively.
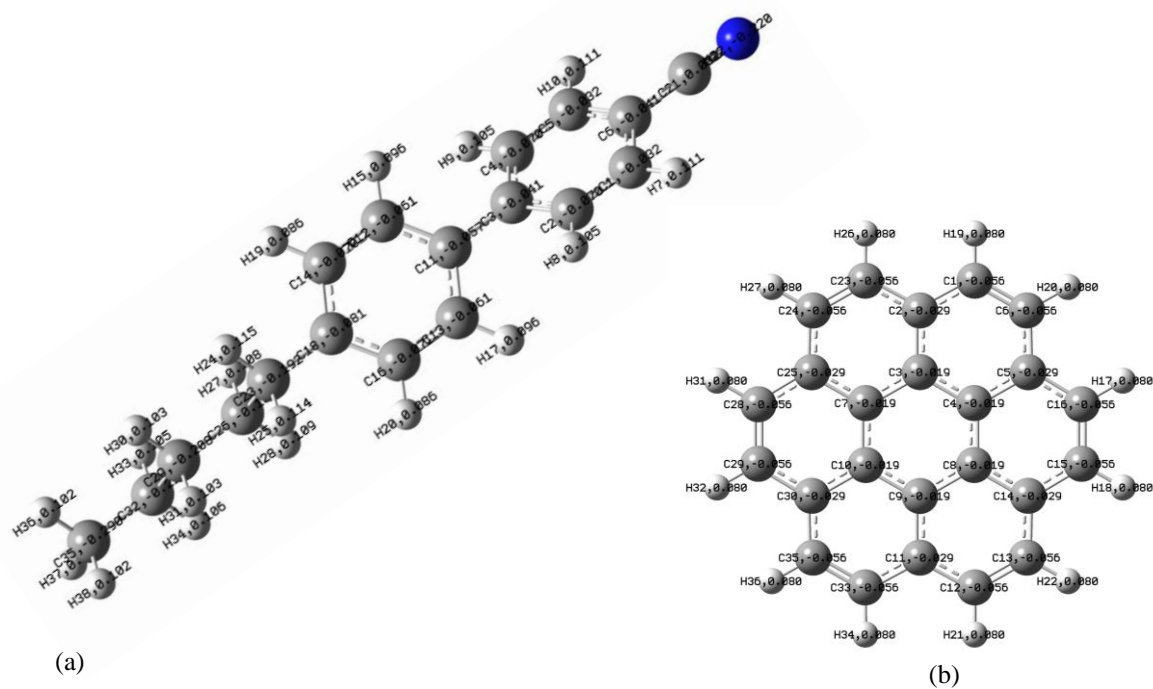

(a)

(b)

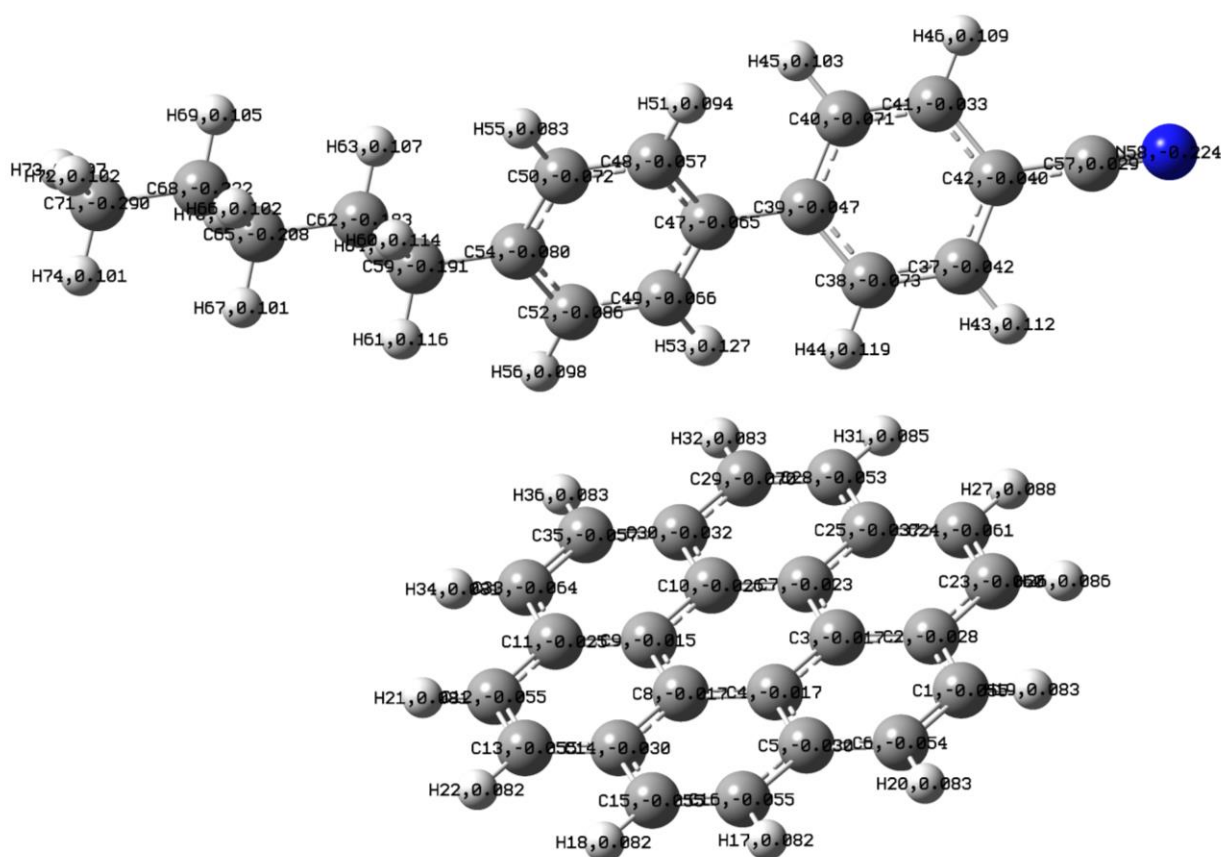**Figure:1-** Optimized geometries (a) 5CB and (b) Coronene molecules

Figure:2- Optimised geometry of the combined system (5CB + coronene)

3.2 Electronic Properties

The distance between the lowest vacant molecular orbital and the highest occupied molecular orbital is known as the energy gap. This characteristic is crucial since it enables us to understand the molecules' stability and reactivity. We have calculated the E_{HOMO}, E_{LUMO}, and other characteristics, including the electron affinity (E.A.) and ionisation potential (I.P.). All of these parameters may be calculated using Koopman's theorem [24,25].

$$IP = -E_{HOMO} \quad \text{and} \quad EA = -E_{LUMO}$$

$$Electroneg ativity (\chi) = -\frac{1}{2}(E_{LUMO} + E_{HOMO}) = -\mu$$

$$\text{Chemical potential } (\mu) = \frac{1}{2}(E_{LUMO} + E_{HOMO})$$

$$\text{Global Hardness } (\eta) = \frac{1}{2}(E_{LUMO} - E_{HOMO})$$

$$\text{Softness } (\varsigma) = \frac{1}{\eta}$$

$$\text{Energy gap } (E_g) = E_{LUMO} - E_{HOMO}$$

$$\text{Electrophilicity index } (\omega) = \frac{\mu^2}{2\eta}$$

Table1:- Global reactivity parameters of 5CB, Coronene and 5CB+Coronene molecules (in eV)

Global Reactivity Parameters	5CB	Coronene	5CB+Coronene
Homo	-6.5683	-5.7030	-5.8738
Lumo	-1.8477	-1.6834	-1.8599
Band gap (eg)	4.7206	4.0196	4.0139

Chemical potential (μ)	-4.2080	-3.6932	-3.8669
η	2.3603	2.0098	2.0070
S	0.2118	0.2488	0.2491
ω	3.7511	3.3933	3.7253
ΔNmax	1.7828	1.8376	1.9267

The chemical potential, global hardness, softness, energy gap, electronegativity, and electrophilicity index are tabulated in Table 1. The Ionization potential indicate the amount of energy required remove an electron from a molecule. The higher value of the ionisation potential shows greater stability of the molecule, while a small value of the ionisation potential indicates high reactivity of the molecules. The value of electron affinity refers to the amount of energy emit when an electron is added to a neutral molecule. The electronegativity of the molecules measures their ability to attract electrons. Chemical hardness is the resistance to change or deformation. Softness and chemical hardness are important concepts to understand the behaviour of chemical systems [25].
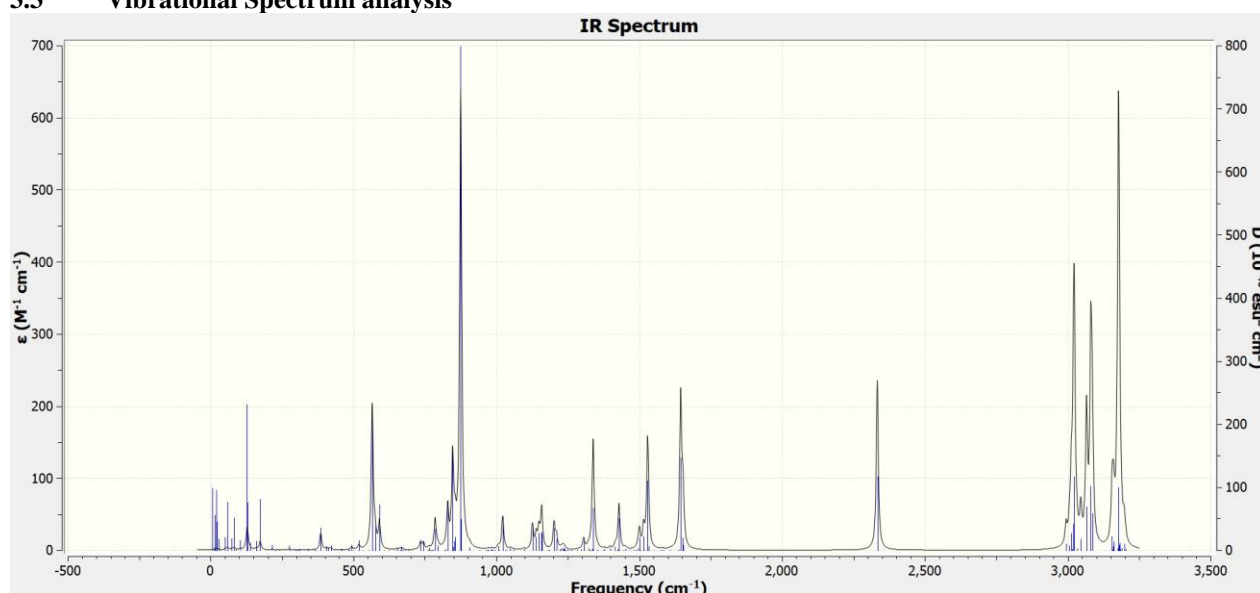
3.3   Vibrational Spectrum analysis

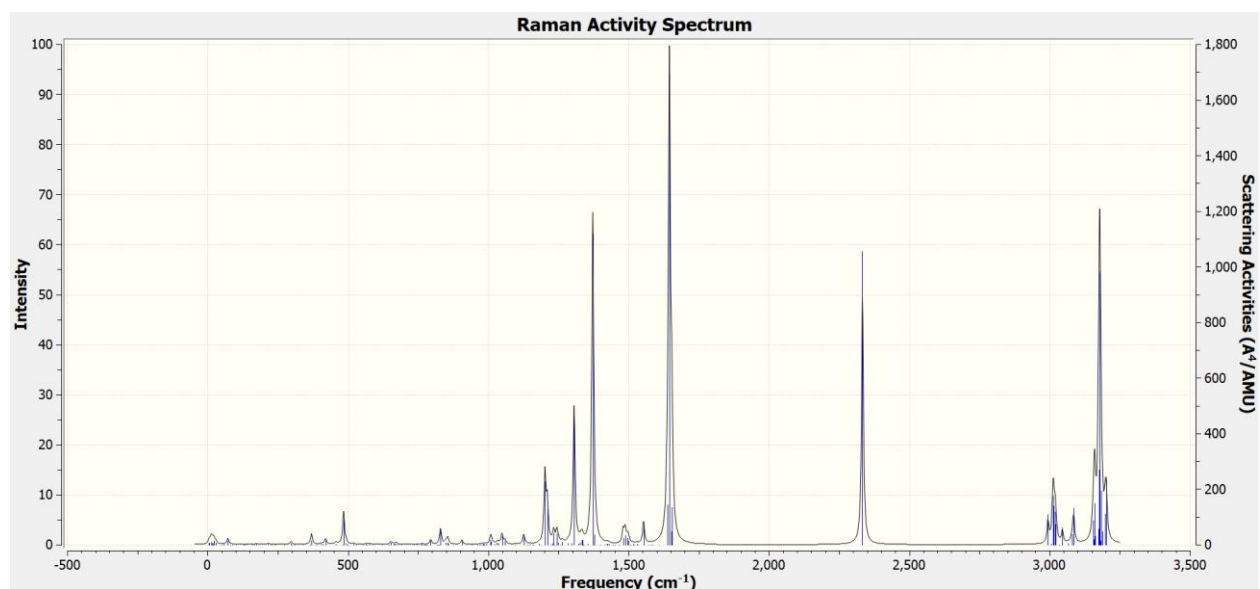**Figure:3-** IR spectra of the combined system (5CB + coronene)

Figure:4- Raman activity of the combined system (5CB + coronene)

The vibrational frequency calculations have been carried out after optimising molecular geometry using the DFT method with the same basis set 6-311G(d,p). The qualitative association of bands and specific structures or chemical groups is a basic interpretation of vibrational spectra. The computed vibrational frequencies/wavenumbers, IR intensities, and Raman activities corresponding to the different normal modes are used to identify the vibrational modes unambiguously. The use of harmonic approximation for the prediction of vibrational frequencies suffers from overestimation of values due to the negligence of anharmonicity in a real system [26–29]. However, the electron–electron interaction term in DFT method makes the frequency value smaller to some extent. The potential energy distributions reveal that most of the normal modes are superposed to several different vibrations. Hence, it is difficult to assign a normal mode of a particular stretching or bending vibration. The calculated IR and Raman of the composite system have been presented in Figs. 3 and 4 respectively.

IV. Conclusions

The electronic and vibrational properties of 5CB, coronene, and 5CB + coronene molecules have been studied. Our target was to investigate the effect of coronene on the original compound. Electronic properties such as electronegativity, chemical potential, global hardness, and softness of composite molecules have higher values compared to the pure 5CB molecule, showing the stability of composite molecules. The variation of HOMO-LUMO energy gap shows the variable charge transfer for composite molecules. The obtained results lead us to believe that composite molecules are better organic electro-optical materials for the design of various electro-optical as well as optoelectronic devices such as photovoltaic cells and solar cells. OLEDs and FET, all-optical switches, bistable and meta devices. The IR peaks and Raman activity peaks were explained.

Acknowledgement

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