

Spectroscopic and FMO Studies of Cholesteryl Stereate Complexes for Electrooptical Activity

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Computational studies have attracted lots of attention to understand the structural behavior of the molecules. Computational techniques grade complex systems for novel properties with new predictions in the areas of physics, chemistry and biology, that would be useful for conducting experiments. Nowadays, Nanoparticle technology, in general, and metal oxide nanoparticles, in particular, have become an integral part in many areas of science. To understand the role of nanoparticles in physico-chemical processes, iron, zinc, aluminum and copper oxide nano particles were conjugated with cholesteryl stereate, and then ultrasonicated to produced desired clusters. Infrared and Raman spectra confirm bonding between cholesteryl stereate and metal oxide nanoparticles. Computational studies of cholesteryl stereate complexes with Gaussian 03 were performed to determine the properties of dipole moment, energy gap, electrophilicity index, polarisability and first order hyperpolarizability that are responsible for electro-optical activity. Interestingly, iron oxide and zinc oxide metal nano particles showed more significant contribution in electro-optical activity compared to that for copper and aluminum oxide nano particles.

Keywords: Cholesteryl stereate, DFT, FTIR, Electro-optical activity

INTRODUCTION

Cholesteryl stereate is an ester of cholesterol and a stearic acid with lower solubility that has gained importance in biological phenomena due to its hydrophobic nature. Studies of physical, chemical properties and solubility of these esters [1] has larger role in oxidation [2], modification of composition in nano emulsions [3], interactions with monomer [4] and changes in thermodynamic and structural parameters of monoclinic systems [5]. Functional importance in formation of structure influenced the complexes of cholesteryl stereate in processing of food with β lactoglobulin [6], modification of starch [7] and amylose [8] during starch gelatinization. Metal stereate complexes have shown their potential in conductance [9], self

assembling [10] and charge transfer [11] processes. The metallic nano particles have generally shown their potential applications in the areas of biology and medicine [12-13], increase the rate of reaction in drug delivery systems, gene delivery with iron [14], zinc [15], copper [16] and aluminum [17]. Concentration of nano particles [18] significantly changes the cytotoxicity and reactivity in the formation of cholesteryl stereate complex.

The focus of the present study is to analyze the behavior of cholesteryl stereate (CS) with metal oxide nano particles iron (IO), zinc (ZNO), aluminum (ALO) and copper (CUO) in formation of complexes CSIO, CSZNO, CSALO and CSCUO bonded structures as illustrated in Fig. 1. Complexes of stereate were studied through FMO and electro-optical property analyses with computational method.

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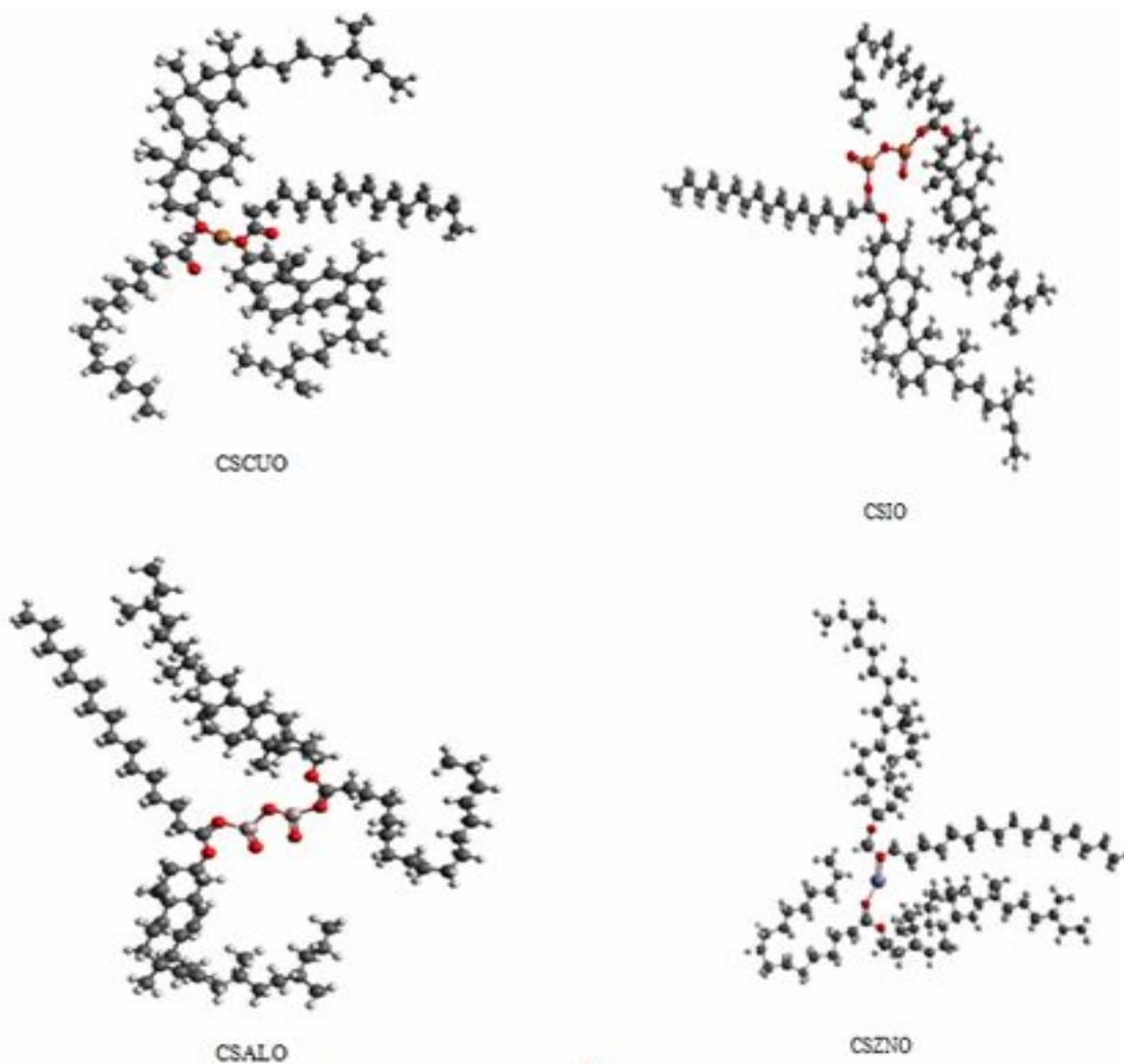


Fig. 1. Bonded structures of sterate complexes.

MATERIALS AND METHODS

Synthesis

Cholesteryl stearate (CS) and nano particles of metallic oxides (IO, ZNO, ALO and CUO) were purchased from Sigma Aldrich and used without further purification. 0.08 mg of iron and aluminum oxide nano particles were synthesized with 500 mg of CS. In addition, 0.06 mg of zinc and copper oxide nanoparticles were synthesized with 500 mg of CS.

The complexes CSIO, CSZNO, CSALO and CSCUO were formed by dissolving with ethanol solution using ultrasonication. The Pci analytics with a 12 mm probe, operating at a frequency of 50 Hz and 220 V, was used in ultrasonication. These sterate complexes were allowed to dry for four days to obtain yield of high purity.

Experimental Studies

Vibration spectral studies were performed using FTIR (Thermo-Nicolet 6700) and FT Raman (BRUKER RFS27)

Table 1. Molecular Properties of Stereate and Corresponding Complexes

Name of the compound	Number of atoms (N)	Number of bonds	Normal modes (3N-6)	Molecular formula
CS	127	130	384	C ₄₅ H ₈₀ O ₂
CSIO	261	268	798	C ₉₀ H ₁₆₀ Fe ₂ O ₇
CSZNO	257	264	786	C ₉₀ H ₁₆₀ ZnO ₄
CSALO	259	256	762	C ₉₀ H ₁₆₀ Al ₂ O ₇
CSCUO	255	262	780	C ₉₀ H ₁₆₀ CUO ₄

for stereate and its complexes. Powdered x-ray diffraction studies with Bruker AXS D8 Advance confirm crystallite size in agreement with specified particles sizes as purchased.

Quantum Chemical Calculation

Optimized geometrical structures with Molecular Editor Avagadro signifies change in molecular properties in stereate and its complexes as listed in Table 1. On optimizing the complexes of stereate the number of atoms, bonds and normal modes were enhanced in comparison with stereate. Monoclinic structure of stereate is changed with increase in the number of bonds, bond lengths and bond angles. With enhancement in molecular properties of complexes an attempt in interpreting spectroscopic and FMO (Frontier molecular orbitals) contours were made with B3LYP functional and MP2 method using Gaussian 03, with 6-31G(d) basis set. Choice of this electron density method (B3LYP functional) signifies influence each electron along with its correlation while in wave function method (MP2) linear combination of state functions are employed. These methods are accurate and similar results are achieved, however, computational time is lesser in B3LYP functional than that in MP2 method.

RESULTS AND DISCUSSION

Experimental studies with FTIR confirm the bonding nature of stereate with metal oxide nano particles due to

shifts in wave numbers and sharp peaks in both functional and finger print regions. Spectral studies of stereate (CS) and stereate complexes (CSIO, CSZNO, CSALO and CSCUO) reveal wave numbers in the range of 400-4000 cm⁻¹, illustrated in Fig. 2. The prominent peaks at 2917, 1415, 1255 and 840 cm⁻¹ correspond to cholesteryl stereate. Studies of stereate complexes reveal downward shifts in C-H stretching and bending, and an upward shift of 40 cm⁻¹ in CH₂ bending. A pronounced downward shift in CSALO and CSCUO and comparable upward shift in stretching with C-O stretching vibration with CSIO and CSZNO is observed. These shifts in wave numbers are attributed to the bonding nature between stereate with metal oxide nano particles in formation of stereate complexes. There is no pronounced change in wave numbers of C=C stretching and CH₃ bending.

Raman spectral studies were performed for further validation on vibration mechanism for stereate and its complexes. Wave numbers of Raman spectra in assigned regions were approximately equal with those of FTIR method. These methods have been compared in Fig. 3 based on their wave numbers.

Quantum chemical studies [19] were performed using Gaussian 03 with B3LYP functional and MP2 method. These studies indicate that (i) there is not any intermediate transition, (ii) computed wave numbers, illustrated in Figure 4, exhibit similar behaviors to those of experimental spectra, (iii) as indicated in Figs. 3 and 4, quantum chemical results are in agreement with experimental studies.

Contours of frontier molecular orbitals [20-21] specify

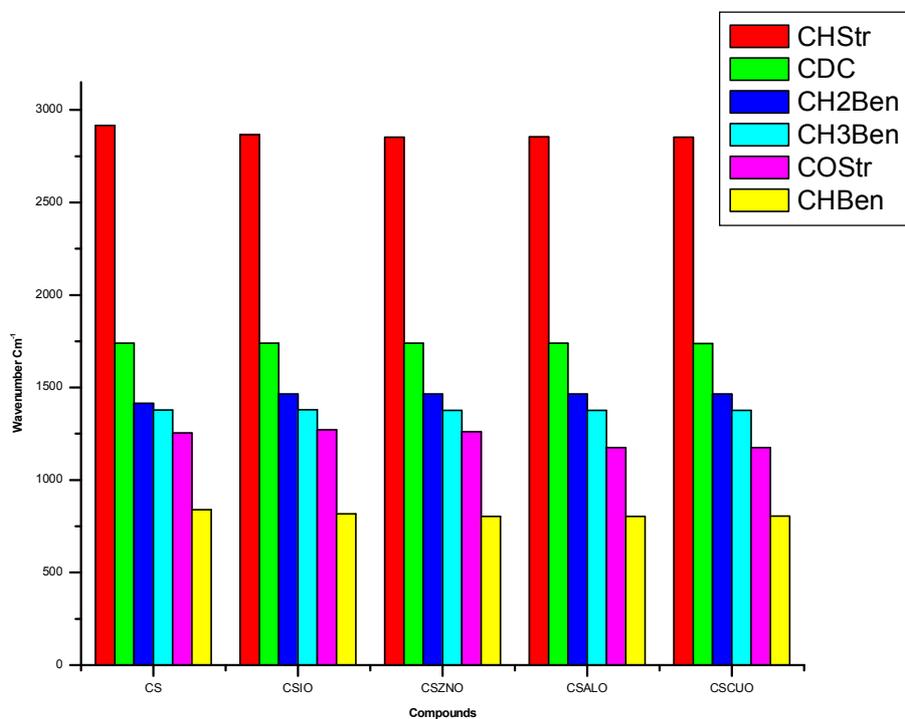


Fig. 2. Illustration of FTIR spectra.

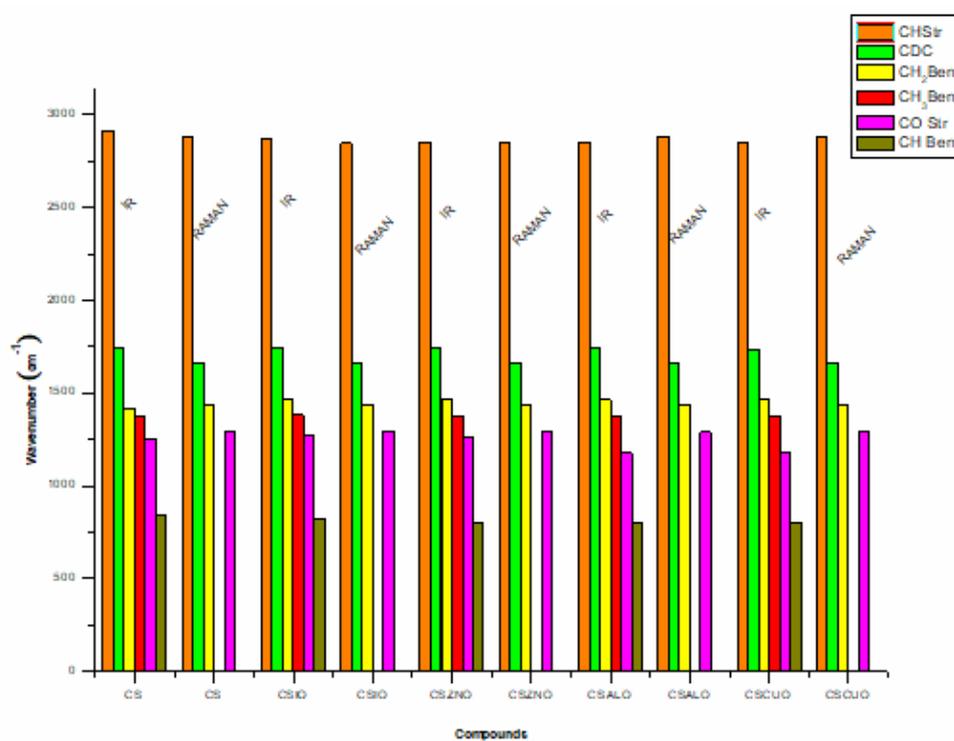


Fig. 3. FTIR and Raman wave numbers of CS and its complex.

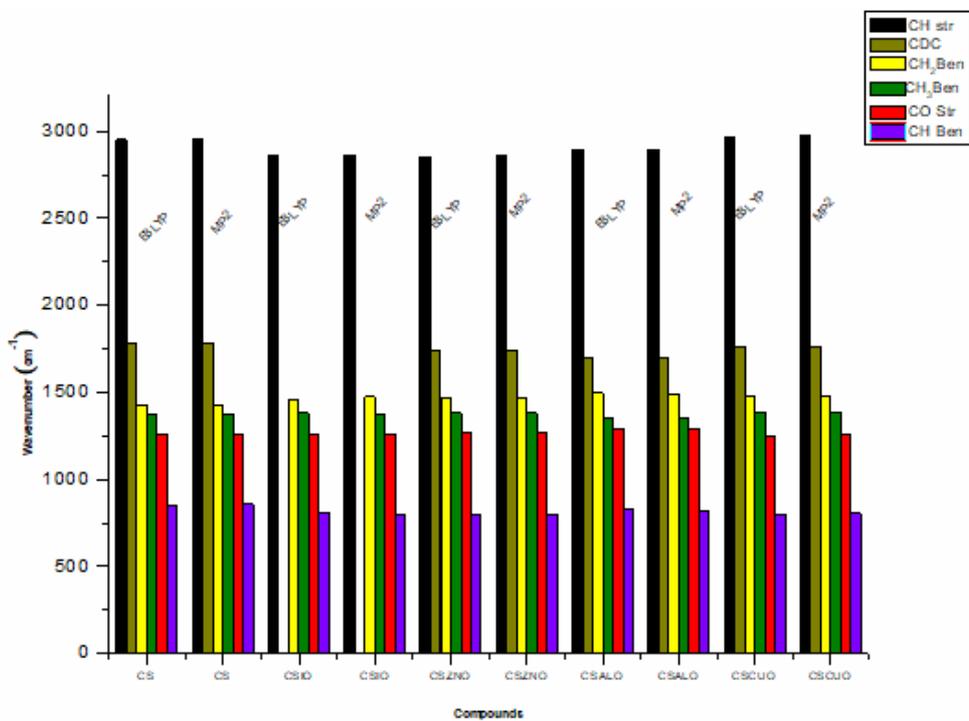


Fig. 4. Computed wave numbers of CS and Complexes.

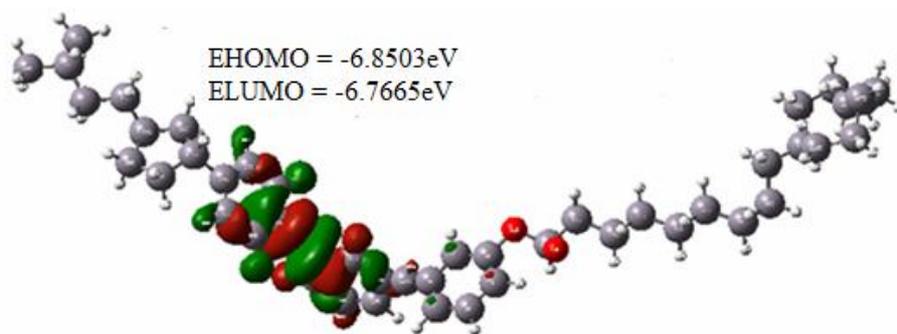


Fig. 5. FMO contour of CS.

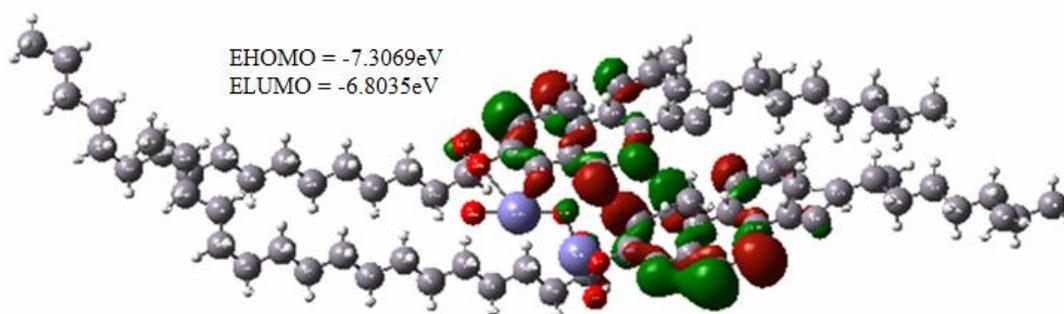


Fig. 6. FMO contour of CSIO.

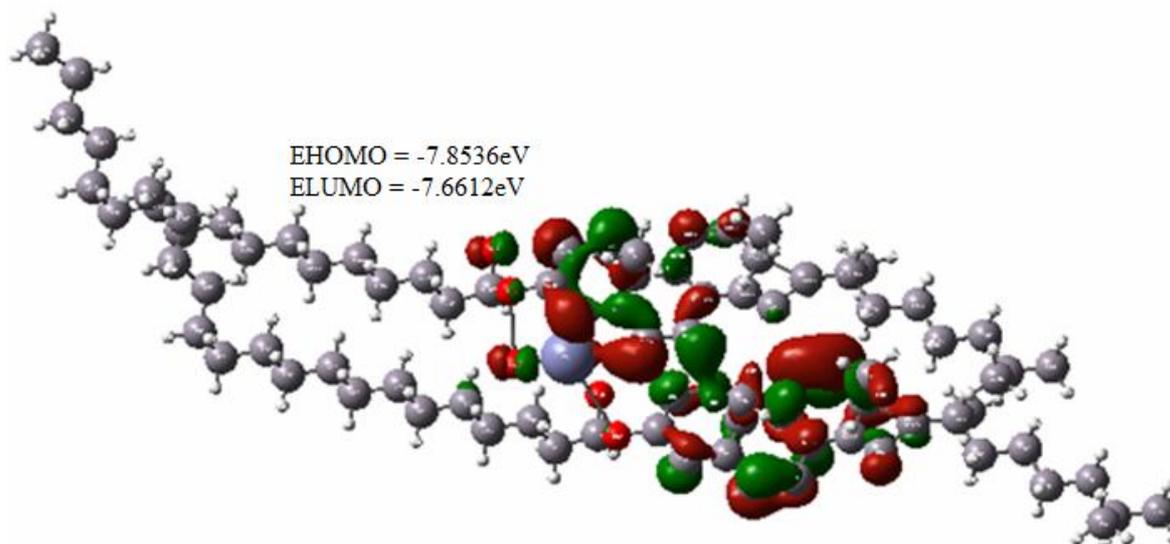


Fig. 7. FMO contour of CSZNO.

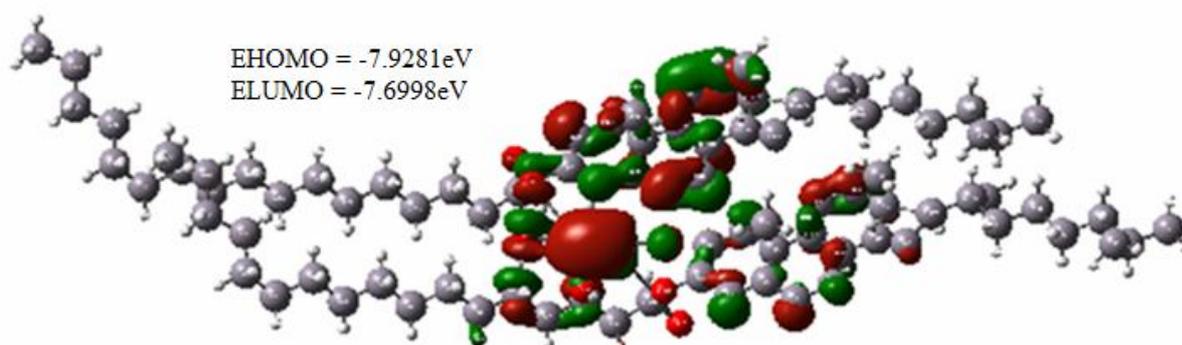


Fig. 8. FMO contour of CSALO.

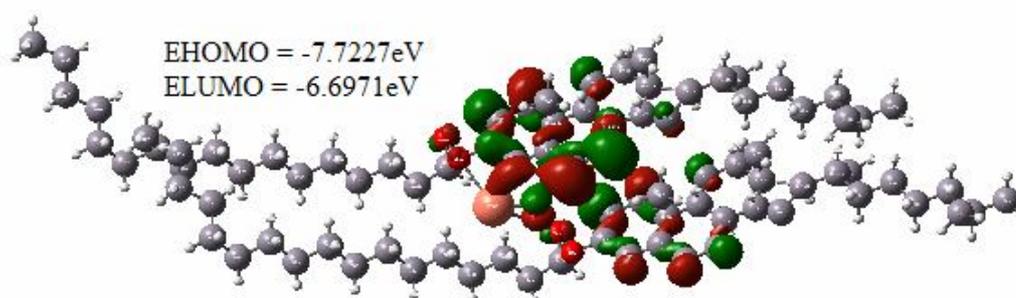


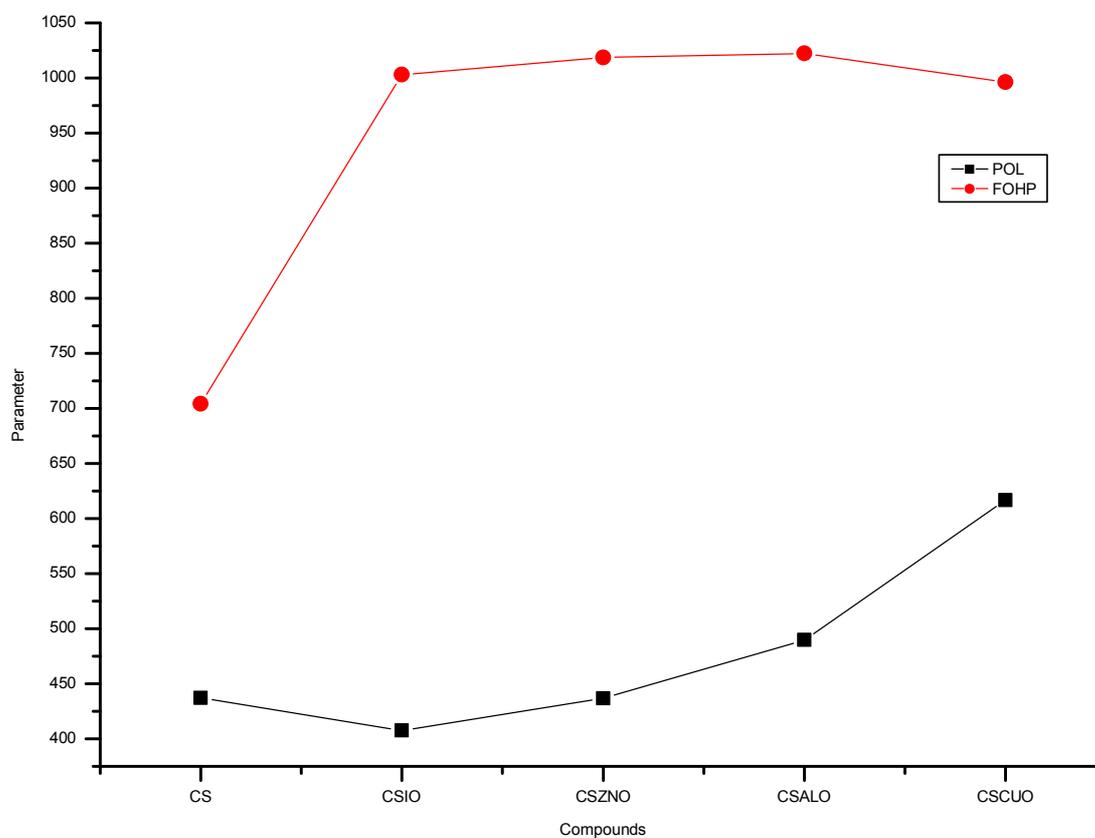
Fig. 9. FMO contour of CSCUO.

gradient of colored portions with red as negatively and green as positively charged areas. These red contours concerns to the LUMOs (lowest unoccupied molecular

orbitals) that are electron donating, and green contours concerns to the HOMOs (highest occupied molecular orbitals) that are electron accepting. Contours of cholesteryl

Table 2. Computed Spectroscopic Properties of Stereate and Complexes

Name of the compound	ΔE (eV)	ρ (Debye)	η (eV)	μ (eV)	$\chi = -\mu$ (eV)	ω (eV)	$\Delta\alpha$ (a.u.)	β (a.u.)
CS	0.0835	7.4946	0.041	-6.8084	6.8084	565.29	437.024	704.18
CSIO	0.5034	7.9845	0.2517	-7.0552	7.0552	98.879	407.46	1003.2
CSZNO	0.1923	7.5593	0.096	-7.7574	7.7574	313.42	436.92	1018.7
CSALO	0.2182	6.4942	0.1091	-7.8090	7.8090	279.47	489.596	1022.3
CSCUO	0.5300	6.2925	0.2650	-6.9622	6.9622	91.457	616.718	996.22

**Fig. 10.** Electrooptical properties of stereate and its complexes.

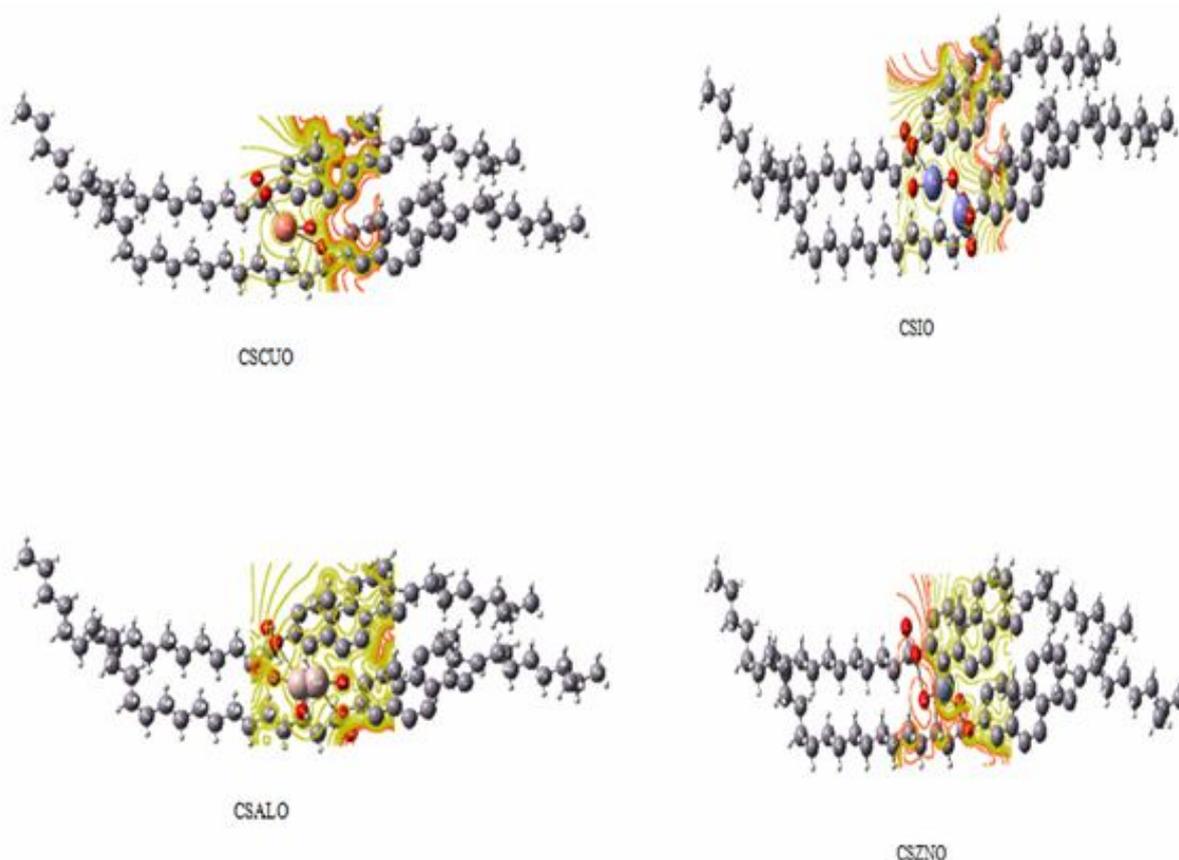


Fig. 11. ESP Contours of sterate complexes.

sterate and its complexes are shown in Figs. 5-9.

The positively charged species (green), having vacant orbitals and attract electrons, are nucleophilic sites that form a chemical bonds with electrophilic sites. In formation of sterate complexes with metal oxide, nano particles act as the active centers for exchange of electrons responsible for non covalent interactions, leading to an increase in energy gaps, hardness, and reactivity. Interestingly, central parts of the FMO contours are more influential than ending parts. Effects of metal nanoparticles on sterate complexes were primarily examined through molecular properties in formation of its structure. Effects of electron correlation are studied in analyzing chemical properties, [22] such as electro negativity, energy gap (ΔE), dipole moment (ρ), chemical hardness (η), chemical potential (μ), susceptibility ($\chi = -\mu$), and electrophilicity index $\omega = \eta^2/2\mu$ of the representative molecules with Koopmann's theorem [23]. Dipole moment refers to the change in molecular energies

pertained to E_{HOMO} and E_{LUMO} of energy gap [24-27] that determine anisotropy of polarization ($\Delta\alpha$) and first order hyperpolarizability β , in atomic units (a.u.), as listed in Table 2 with suitable expressions.

An increase in energy gap indicates the stable state of sterate with chemical hardness. Complexes of CSIO and CSZNO were more reactive with increased dipole moment with nature of molecule to be polar and reactive than CSALO and CSCUO. There is an enhancement in chemical potential that is inversely proportional to electrophilicity index. Total polarization has been significantly altered in complexes of CSALO and CSCUO compared to that of CSIO and CSZNO. A significant feature is electro-optical property is the first order hyperpolarizability enhanced in complexes of metal oxide nano particles in comparison with cholesteryl sterate, as illustrated in Fig. 10.

Electrostatic potential (ESP) contour maps represent the electron density distribution, shown with colored lines. The

red color lines concern to the areas with the most probable distribution. This probability is reduced as the contour lines change to yellow, green and blue. ESP contours of stereate and complexes are shown in Fig. 11. As shown in this figure, the high probability of contours in central zone (red color) has changed to there is yellow, indicating the electrophilic activity with an increase in potential.

CONCLUSIONS

Metal oxide nano particles have caused some changes in molecular structure leading to the change in molecular properties. Significant change in wave numbers with sharp peaks, in assigned regions, confirms bonding between cholesteryl stereate and metal oxide nanoparticles. Computational studies do not predict any intermediate transition. Additionally, wave numbers are very close to those obtained through experiments. Significant change in dipole moment, polarization and first order hyperpolarizability are responsible for electro-optical activity. On the basis of contour maps, electron probability distribution is responsible for electro-optical activity. These significant changes indicate that stereate complexes with non covalent interactions are structurally active anisotropic biomaterials.

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