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Experimental (FT-IR, FT-Raman, UV-vis spectra) and theoretical (RHF and DFT) investigation and NBO analysis on the structure of sustiva (EFV) HIV drug

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ABSTRACT

A systematic vibrational spectroscopic assignment and analysis of sustiva(EFV) has been carried out by using FTIR, FT-Raman and UV spectral data. The vibrational analysis were aided by electronic structure calculations – ab initio (RHF) and hybrid density functional methods (B3LYP) performed with 6-31G(d,p) and 6-31++G(d,p) basis sets. Molecular equilibrium geometries, electronic energies, bond orders, natural bond order analysis, IR intensities, and harmonic vibrational frequencies have been computed. The assignments proposed based on the experimental IR and Raman spectra have been reviewed and selected assignment of the observed spectra have been proposed. UV–visible spectrum of the compound was also recorded and the electronic properties, such as HOMO and LUMO energies and λ_{max} were determined by time-dependent DFT (TD-DFT) method. The thermodynamic functions of the title molecule were also performed using the RHF and DFT methods.

Introduction

Sustiva(EFV) belongs to the class of the non-nucleoside reverse transcriptase inhibitors. Sustiva(EFV) exerts its action by non-competitive inhibition of the human immunodeficiency virus type 1 (HIV-1) reverse transcriptase. HIV-2 reverse transcriptase and human cellular DNA polymerases are not inhibited by sustiva(EFV) [1]. Treatment of patients with sustiva(EFV) monotherapy rapidly selects for resistant isolates of HIV-1 with the mutation at reverse transcriptase amino acid position 103 (lysine to asparagine) being most frequently observed [1,2]. However, when administered in combination with nucleoside reverse transcriptase inhibitors and protease inhibitors, sustiva (EFV) has demonstrated a potent antiviral effect and is therefore an important addition to the currently available armamentarium of antiretroviral drugs [3–6].

In our present work, an attempt has been made to interpret the vibrational spectra of sustiva(EFV) by applying ab initio and density functional theory calculations based on Hartree-Fock and Becke3- Lee-Yang-Parr (B3LYP) level using 6-31G(d,p)and 6-31++G(d,p) basis sets. Further, the calculation of electronic excitations, particularly for valence-like transitions and oscillator strength of sustiva (EFV), were calculated employing the all valence electron TD-DFT methods. In addition to these bond orders and atomic charges calculated at the HF/6-31G(d,p), HF/6-31++G(d,p), B3LYP/6-31G(d,p) and B3LYP/6-31++G(d,p) levels. Experimentally observed spectral data of the title compound is found to be well comparable with the data obtained by quantum mechanical methods.

Experimental

The solid phase FTIR spectrum was recorded in the region 4000-400 cm^{-1} in evacuation mode on Nexus 670 DTGS using KBr pellet technique with 4.0 cm^{-1} resolution. The FT-Raman spectrum was recorded using 1064 nm line of Nd: YAG laser as excitation wavelength in the region 5000-100 cm^{-1} on Bruker IFS 66V spectrometer equipped with FRA 106 Raman module was used as an accessory. The UV-visible spectrum was recorded on a Varian Cary 5E from the region 360 to 260 nm.

Computational details

To provide complete information regarding the structural characteristics and the fundamental vibrational modes of sustiva(EFV) the restricted Hartree-Fock and DFT-B3LYP correlation functional calculations have been carried out. The calculations of geometrical parameters in the ground state were performed using the Gaussian 03 [7] programs, invoking gradient geometry optimization [8] on Intel core i3/2.93 GHZ processor. The geometry optimization was carried out using the initial geometry generated from standard geometrical parameters at Hartree-Fock level, and B3LYP methods adopting 6-31G(d,p) and 6-31++G(d,p) basis sets to characterize all stationary points as minima. The optimized structural parameters of the compound sustiva(EFV) were used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios. In DFT methods, Becke's three parameter exchange-functional (B3) [9,10] combined with gradient-corrected correlation functional of Lee, Yang and Parr (LYP) [11] by implementing the split-valence polarized 6-31G(d,p) and 6-31++G(d,p) basis sets [12,13] have been utilized for the computation of molecular structure optimization, vibrational frequencies, thermodynamic properties and energies of the optimized structures.

Results and discussion

Molecular geometry

The molecular structure of sustiva(EFV) belongs to C1 point group symmetry. All vibrations are active in both IR and

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Raman. The optimized structure parameters of sustiva(EFV) calculated by HF and DFT-B3LYP levels are listed in the Table 1 in accordance with the given Fig. 1(a) molecular structure and Fig. 1(b) atom numbering scheme of sustiva (EFV). Table 1 compares the calculated bond lengths and angles for sustiva(EFV) with those experimentally available data [14]. From the theoretical values, we can find that most of the optimized bond angles are slightly larger than the experimental values due to the theoretical calculations belonging to isolated molecules in gaseous phase and the experimental results belonging to the molecule in the solid state. Comparing bond angles and lengths of B3LYP/6-31G(d,p) and B3LYP/6-31++G(d,p) with those of HF/6-31G(d,p) and HF/6-31++G(d,p), as a whole the former are on higher side than the latter and the HF calculated values correlates well compared to those with the experimental results. In spite of the differences, calculated geometric parameters represent a good approximation and they are the basis for calculating other parameters, such as vibrational frequencies and thermodynamic properties.

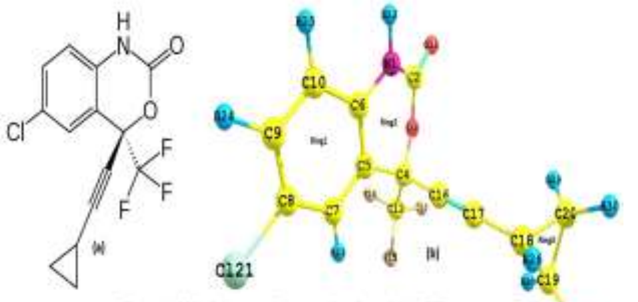


Figure 1. (a) Molecular structure (b) Atom number scheme of sustiva(EFV)

Bond order analysis

The bond order of sustiva(EFV) is presented in Table 2. Bond order is related to bond strength. The bonds with the higher bond order values have short bond length and vice versa. The bond order analysis may predict that the weakest bonds may be cleaved preferentially and they may possess a relatively low pi-bond character. From Table 2, it is noted that bond between C4-C16 possess relatively low pi bond character with low bond order value of 0.79 and 0.80 obtained from HF and B3LYP method respectively. The C2-O11 bond order values are in the range 1.9, which depict the double bond character, while the C8-Cl21 and C4-C12 bond order value is approximately unity, which shows the single bond character. The very strongest bond is C16-C17 with the bond order value of 3.228 and 2.667 predicted from both HF and B3LYP methods confirms the treble bond character. The optimised geometrical values are in support of the bond order analysis.

Electronic properties

The energies of four important molecular orbitals of sustiva(EFV): the highest and second highest occupied MO's (HOMO and HOMO−1), the lowest and the second lowest unoccupied MO's (LUMO and LUMO+1) were calculated and are presented in Table 3. The lowest singlet→singlet spin-allowed excited states of sustiva(EFV) were taken into account for the TD-DFT calculation in order to investigate the properties of electronic absorption. The experimental λ_{max} values are obtained from the UV/visible spectra recorded in methanol. The calculations were also performed with methanol solvent effect. The calculated absorption wavelengths λ_{max}), oscillator strength, excitation energies and the experimental wavelengths are also given in Table 3. The energy gap between HOMO and LUMO is a critical parameter in determining molecular electrical transport properties [15].

In the electronic absorption spectrum of sustiva(EFV), there are three absorption bands with a maximum 298 nm. The strong absorption band 298nm is caused by the $n\rightarrow\pi^*$ and the other two calculated value moderately intense bands are due to $\pi\rightarrow\pi^*$ transitions. The $\pi\rightarrow\pi^*$ transitions are expected to occur relatively at lower wavelength, due to the consequence of the extended aromaticity of the benzene ring. The HOMO and LUMO of sustiva(EFV) are represented in Fig. 2.

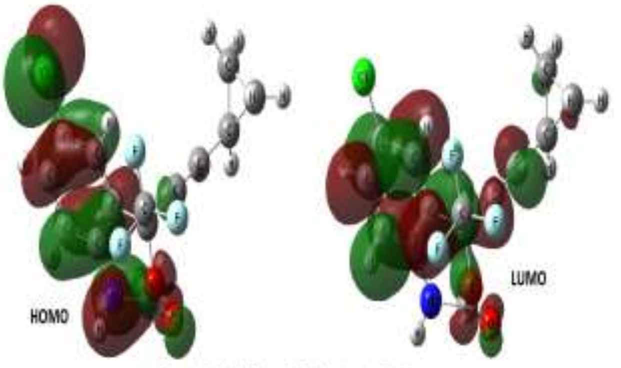


Figure 2. The HOMO and LUMO of sustiva(EFV)

Natural population analysis

The calculation of effective atomic charges plays an important role in the application of quantum mechanical calculations to molecular systems. Our interest here is in the comparison of different methods (HF/6-31, HF/6-31++, DFT-B3LYP/6-31 and DFT-B3LYP/6-31++) to describe the electron distribution in sustiva(EFV) as broadly as possible, and to assess the sensitivity of the calculated charges to changes in the choice of the quantum chemical method. The calculated natural atomic charge values from the natural population analysis (NPA) and Mulliken population analysis (MPA) procedures using the HF/6-31, HF/6-31++, DFT-B3LYP/6-31 and DFT-B3LYP/6-31++ methods are listed in Table 4. The NPA from the natural bonding orbital (NBO) method is better than the MPA scheme. Table 4 compares the atomic charge site of sustiva(EFV) from both MPA and NPA methods. The NPA of sustiva(EFV) shows that the presence of two oxygen atoms [O3 = -0.635 (HF/6-31), -0.632(HF/6-31++), -0.560(DFT-B3LYP/6-31) and -0.553(DFT-B3LYP/6-31++); O11= -0.619(HF/6-31), -0.614(HF/6-31++), -0.516(DFT-B3LYP/6-31), and -0.516(DFT-B3LYP/6-31++)] imposes large positive charges on the carbon atom [C2 = 1.142 (HF/6-31), 1.127(HF/6-31++), 0.961(DFT-B3LYP/6-31) and 0.947(DFT-B3LYP/6-31++)]. However, the nitrogen and oxygen atoms N1 and O3 possess large negative charges, resulting in the positive charges on the carbon atoms C2, C5, C6 and C12. Moreover, there is no difference in charge distribution observed on all hydrogen atoms except the H22 hydrogen atom (H22= 0.466, 0.464, 0.453 & 0.456 in HF/6-31, HF/6-31++, DFT-B3LYP/6-31 and DFT-B3LYP/6-31++ respectively. The large positive charge on H22 is due to the large negative charge accumulated on the N1 atom.

Vibrational analysis

The FTIR and FT-Raman spectra of sustiva(EFV) are shown in **Fig**s. 3 and 4. The observed and calculated frequencies using HF/6-31G(d,p), HF/6-31++G(d,p), B3LYP/6-31G(d,p), and B3LYP/6-31++G(d,p) methods along with their relative intensities and assignments of sustiva(EFV) are summarised in Table 5. The maximum number of values determined by HF/6-31G(d,p) method is well agreed with the experimental values and is also confirmed by the scale factors used to get the scaled frequencies. Therefore, this method is considered to be more reliable and taken for discussion. The calculated (HF & B3LYP)methods vibrational spectra were shown in Fig. 5.

Table 1. Structural parameters of Sustiva(EFV) calculated by HF and B3LYP methods using 6-31G(d,p) and 6-31++G(d,p) basis sets

Structural parameters	Sustiva(EFV)									
	B3LYP/ 6-31G(d,p)	B3LYP/ 6-31++G(d,p)		HF/ 6-31G(d,p)	HF/ 6-31++G(d,p)		Exp[14]			
Internuclear distance (A°)										
N1-C2	1.38	1.38		1.36	1.36		1.45			
N1-C6	1.40	1.40		1.39	1.39		1.40			
N1-H22	1.01	1.01		0.99	0.99		1.01			
C2-O3	1.36	1.36		1.34	1.34		1.42			
C2-O11	1.21	1.21		1.18	1.18		1.21			
O3-C4	1.46	1.46		1.42	1.42		1.43			
C4-C5	1.53	1.53		1.53	1.53		1.50			
C4-C12	1.55	1.56		1.54	1.54		1.52			
C4-C16	1.46	1.46		1.47	1.47		1.47			
C5-C6	1.40	1.40		1.39	1.39		1.39			
C5-C7	1.39	1.40		1.39	1.39		1.40			
C6-C10	1.40	1.40		1.39	1.39		1.40			
C7-C8	1.39	1.39		1.38	1.38		1.39			
C7-H23	1.08	1.08		1.07	1.07		1.10			
C8-C9	1.39	1.40		1.38	1.38		1.39			
C8-Cl21	1.76	1.76		1.74	1.74		1.72			
C9-C10	1.39	1.39		1.38	1.38		1.40			
C9-H24	1.08	1.08		1.07	1.07		1.10			
C10-H25	1.09	1.09		1.08	1.08		1.10			
C12-F13	1.34	1.34		1.31	1.31		1.39			
C12-F14	1.34	1.35		1.32	1.32		1.39			
C12-F15	1.35	1.35		1.32	1.32		1.39			
C16-C17	1.21	1.21		1.19	1.19		1.21			
C17-C18	1.44	1.44		1.45	1.45		1.54			
C18-C19	1.52	1.53		1.51	1.51		1.50			
C18-C20	1.53	1.53		1.51	1.51		1.50			
C18-H26	1.09	1.09		1.08	1.08		1.09			
C19-H27	1.09	1.09		1.08	1.08		1.09			
C19-H28	1.08	1.08		1.07	1.07		1.09			
C20-H29	1.08	1.08		1.07	1.07		1.09			
C20-H30	1.09	1.09		1.08	1.08		1.09			
Bond angle (◦)										
C2-N1-C6	124.1	124.2		123.7	123.6		114.4			
C2-N1-H22	114.1	114.5		114.5	114.7		116.2			
C6-N1-H22	119.6	119.7		119.9	119.9		118.2			
N1-C2-O3	114.8	114.9		114.7	114.8		114.3			
N1-C2-O11	123.8	123.9		123.8	123.8		124.6			
O3-C2-O11	121.3	121.1		121.6	121.4		120.3			
C2-O3-C4	120.3	120.6		122.0	122.3		121.5			
O3-C4-C5	110.3	110.3		110.2	110.3		109.3			
O3-C4-C12	101.6	101.2		102.0	101.8		102.3			
O3-C4-C16	110.3	110.3		110.3	110.3		111.6			
C5-C4-C12	113.3	113.4		113.6	113.6		112.4			
C5-C4-C16	110.7	110.8		110.7	110.7		109.3			
C12-C4-C16	110.3	110.3		109.8	109.8		109.6			
C4-C5-C6	115.5	115.6		115.3	115.4		114.2			
N1-C6-C10	121.3	121.1		121.1	120.9		120.2			
C5-C6-C10	120.3	120.3		120.4	120.4		119.1			
C5-C7-C8	119.5	119.6		119.6	119.7		120.1			
C8-C7-H23	119.8	119.6		119.4	119.3		119.9			
C7-C8-C9	121.2	121.1		120.9	120.9		119.9			
C7-C8-Cl21	119.3	119.3		119.4	119.4		120.1			
C9-C8-Cl21	119.6	119.6		119.7	119.6		120.1			
C8-C9-C10	119.3	119.3		119.6	119.5		120.0			
C8-C9-H24	120.2	120.3		120.1	120.2		120.0			
C10-C9-H24	120.5	120.4		120.3	120.3		120.0			
C6-C10-C9	120.1	120.1		119.9	119.9		120.6			
C6-C10-H25	119.9	120.0		120.1	120.1		119.7			
C9-C10-H25	120.0	120.0		120.1	120.0		119.7			

C4-C12-F13	110.9	111.1		110.9	111.0		110.5			
C4-C12-F14	111.1	111.3		110.9	111.0		109.5			
C4-C12-F15	110.5	110.9		110.9	111.1		110.2			
F13-C12-F14	108.6	108.2		108.4	108.2		109.5			
F13-C12-F15	107.7	107.4		107.7	107.6		106.3			
F14-C12-F15	108.0	107.7		107.9	107.8		107.2			
C17-C18-C19	119.9	119.9		119.5	119.5		120.0			
C17-C18-C20	119.8	119.8		119.4	119.4		120.0			
C18-C19-H27	116.7	116.6		116.9	116.8		115.8			
C18-C19-H28	117.0	116.9		117.3	117.3		117.2			
C20-C19-H27	118.8	118.8		118.6	118.6		120.0			
H27-C19-H28	114.9	115.0		114.8	114.9		113.2			
C18-C20-H30	116.7	116.5		116.9	116.8		115.2			
C19-C20-H29	118.3	118.2		118.2	118.2		120.0			
C19-C20-H30	118.8	118.8		118.6	118.6		118.5			

Table 3. Experimental and calculated absorption wavelenght(λ), excitation energies(E), oscillator strength(f) and frontier orbital energies of sustiva(EFV) by TD-DFT method

λ(Expt.;nm)	λ(Cal.;nm)	E(eV)	f	Assignment	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{HOMO-1} (eV)	E_{LUMO+1} (eV)
298	304.43	4.8826	0.0359	$n\rightarrow\pi^{*}$	-6.0666	-1.1840	-6.9607	-0.6297
	264.50	5.7768	0.0455	$\pi\rightarrow\pi^{-*}$				
	242.75	6.3311	0.1230	$\pi\rightarrow\pi^{*}$				

Table 4. Natural atomic charges of Sustiva(EFV)

	MPA				NPA			
Atom	B3LYP/ 6-31G(d,p)	B3LYP/ 6-31++G(d,p)	HF/ 6-31G(d,p)	HF/ 6-31++G(d,p)	B3LYP/ 6-31G(d,p)	B3LYP/ 6-31++G(d,p)	HF/ 6-31G(d,p)	HF/ 6-31++G(d,p)
N1	-0.632	-0.432	-0.804	-0.538	-0.698	-0.691	-0.787	-0.778
C2	0.710	0.643	0.983	0.775	0.961	0.947	1.142	1.127
O3	-0.489	-0.172	-0.649	-0.315	-0.560	-0.553	-0.635	-0.632
C4	-0.060	-0.380	0.154	0.318	0.127	0.120	0.184	0.185
C5	0.057	0.045	-0.122	-0.053	-0.101	-0.099	-0.136	-0.134
C6	0.312	0.610	0.356	0.295	0.173	0.166	0.230	0.226
C7	-0.097	-0.601	-0.071	-0.558	-0.217	-0.207	-0.188	-0.176
C8	-0.118	0.068	-0.198	0.152	-0.080	-0.091	-0.088	-0.099
C9	-0.073	-0.162	-0.097	-0.260	-0.227	-0.219	-0.194	-0.184
C10	-0.124	-0.533	-0.180	-0.362	-0.257	-0.249	-0.273	-0.265
O11	-0.387	-0.315	-0.488	-0.413	-0.516	-0.516	-0.619	-0.614
C12	0.868	1.036	1.229	1.218	1.140	1.106	1.305	1.257
F13	-0.267	-0.270	-0.378	-0.384	-0.344	-0.344	-0.403	-0.394
F14	-0.265	-0.282	-0.377	-0.404	-0.346	-0.344	-0.404	-0.395
F15	-0.261	-0.253	-0.385	-0.383	-0.354	-0.351	-0.414	-0.405
C16	0.143	0.063	-0.059	-0.454	-0.110	-0.089	-0.151	-0.161
C17	-0.064	-0.229	-0.080	0.486	0.084	0.077	0.096	0.118
C18	-0.125	0.251	-0.092	-0.180	-0.322	-0.321	-0.307	-0.305
C19	-0.204	-0.582	-0.243	-0.488	-0.474	-0.461	-0.459	-0.439
C20	-0.205	-0.527	-0.242	-0.444	-0.474	-0.462	-0.459	-0.440
Cl21	-0.009	0.271	0.014	0.269	0.017	0.026	-0.002	0.004
H22	0.284	0.370	0.345	0.407	0.453	0.456	0.466	0.464
H23	0.159	0.219	0.252	0.255	0.284	0.283	0.292	0.288
H24	0.111	0.142	0.185	0.165	0.259	0.257	0.257	0.252
H25	0.094	0.107	0.166	0.148	0.246	0.245	0.244	0.240
H26	0.149	0.257	0.192	0.241	0.297	0.293	0.290	0.282
H27	0.117	0.150	0.136	0.116	0.253	0.247	0.243	0.233
H28	0.126	0.175	0.156	0.130	0.266	0.262	0.262	0.254
H29	0.127	0.158	0.147	0.110	0.257	0.252	0.248	0.238
H30	0.124	0.173	0.152	0.148	0.265	0.261	0.260	0.253

Table 5. Selected observed and calculated vibrational assignments of Sustiva(EFV)

Observed wavenumber (cm^{-1})		**Calculated wavenumber(cm-1)**								
		HF/6-31 G(d,p)		**HF/6-31++ G(d,p)**		**B3LYP/6-31 G(d,p)**		**B3LYP/6-31++ G(d,p)**		
FTIR	FTRaman	unscal	scal	unscal	scal	unscal	scal	unscal	scal	Assignments
3527	3091	3893	3680	3888	3675	3644	3459	3639	3455	Ring2[ν(NH)]
3324	3027	3428	3266	3425	3264	3256	3112	3251	3107	Ring1[ν(CH)]
		2555	2471	2540	2457	2349	2279	2335	2266	ν (C≡C)
1749	1749	1793	1756	1787	1750	1642	1612	1636	1607	ν[Ring1+NH2 wagging]
1659	1615	1674	1643	1668	1637	1536	1511	1529	1504	ν[Ring1+NH2 wagging]
1604	1602	1633	1604	1630	1601	1494	1471	1493	1470	ν[Ring1+NH2 wagging]
1498	1500	1518	1494	1512	1488	1401	1381	1395	1375	[ν(Ring3)+CH2 wagging]
1430	1454	1459	1437	1453	1431	1326	1309	1322	1305	δ[CH2]
1323	1363	1350	1332	1345	1327	1243	1229	1216	1202	oop(CH)
1252	1276	1268	1253	1264	1249	1192	1179	1173	1161	[ν(Ring1)+CH2 wagging]
1194	1169	1207	1194	1205	1192	1087	1077	1085	1075	[ν(Ring1)+CH2 scissoring]
1084	1097	1095	1085	1092	1082	994	987	988	981	[ν(Ring1)+CH]
1033	1037	1044	1035	1038	1029	946	940	945	939	[ν(Ring1+Ring2)]
984	927	951	945	948	942	875	870	870	865	[ν(Ring1+Ring2)]
932		931	925	928	922	834	830	831	827	Ring1[ν(CH2)]
881	863	897	892	894	889	825	821	823	819	ν[Ring3]
750	742	763	760	760	757	695	693	692	690	ν [Ring1+Ring2]
663	655	646	645	640	639	583	583	577	577	ν [Ring1+Ring2+Ring3]
556	565	567	567	562	562	522	522	519	519	ν [Ring1+Ring2+Ring3]
470	483	473	473	471	471	429	430	428	429	ν [Ring1+Ring2+Ring3]

ν- stretching, δ - deformation, oop - out of plane

Table 6. The calculated thermodynamic parameters of Sustiva(EFV)

Parameter	**HF/6-31 G(d,p)**	**HF/6-31++ G(d,p)**	**B3LYP/6-31 G(d,p)**	**B3LYP/6-31++ G(d,p)**
Total Energy(a.u)	-1497.11	-1497.14	-1503.56	-1503.61
Zero point energy(Kcal/Mol)	140.085	139.595	129.528	128.929
Rotational Constants(GHz)	0.347	0.345	0.341	0.338
	0.197	0.197	0.194	0.194
	0.184	0.184	0.182	0.182
Entropy				
Translational	43.139	43.139	43.139	43.139
Rotational	34.501	34.508	34.543	34.555
Vibrational	61.376	61.783	68.303	66.484
Dipole moment(Debye)	4.6930	4.9634	4.3503	5.0071

Table 2. Bond orders of Sustiva(EFV)

Bond order	HF/6-31G(d,p)	B3LYP/6-31G(d,p)
N1-C2	0.966	0.983
N1-C6	0.87	0.893
N1-H22	0.869	0.886
C2-O3	0.876	0.932
C2-O11	1.944	1.981
O3-C4	0.85	0.872
C4-C5	0.989	0.945
C4-C12	1.021	0.94
C4-C16	0.793	0.802
C5-C6	1.419	1.389
C5-C7	1.433	1.424
C6-C10	1.406	1.378
C7-C8	1.417	1.378
C7-H23	0.901	0.891
C8-C9	1.412	1.398
C8-Cl21	1.033	1.014
C9-C10	1.466	1.451
C10-H25	0.952	0.934
C12-F13	0.896	1.005
C12-F14	0.894	1.004
C12-F15	0.843	0.945
C16-C17	3.228	2.667
C17-C18	0.886	1.023
C18-C19	0.942	0.95
C18-C20	0.934	0.947
C18-H26	0.936	0.92
C19-C20	0.942	0.969
C19-H27	0.963	0.948
C19-H28	0.957	0.947
C20-H29	0.964	0.951
C20-H30	0.958	0.944

Since the calculated vibrational wave numbers were known to be higher than the experimental ones, they were scaled down by the wavenumber linear scaling procedure of Yoshida et al[16] by using the expression : νobs= (1.0087 − 0.0000163νcalc.) νcalc. Comparison of the frequencies calculated at HF and B3LYP with experimental values (Table 5) reveals the over estimation of the calculated vibrational modes due to the neglect anharmonicity in real system. Inclusion of electron correlation in considering the contribution of the cyclopropyl (ring3) whose (CH2 wagging) stretches are present in the Raman spectra at 1500 cm^{-1}. The δ(CH2) deformation are present in the Raman spectra at 1454 cm^{-1}. The NH wagging mode has been identified at 556 cm^{-1}, and is also in agreement with the computed value. The wave number calculated by the HF/6-31 G(d,p) method at 567 cm^{-1} is identified at 556 cm^{-1} in the FT-Raman spectrum.. Both ring1 and ring2 stretching mode takes place between 984 and 1033 cm^{-1}. Notice that the most evident discrepancies between the experimental and calculated spectra are associated with stretching modes of the amide group, showing its participation in hydrogen bonds. The assumption that the amide group plays very important role in stabilizing the structure of sustiva(EFV).

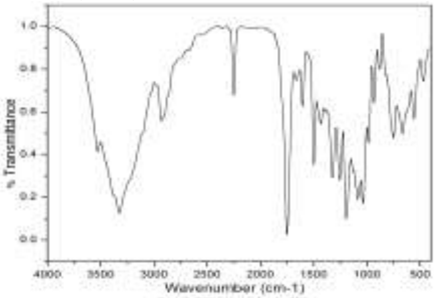
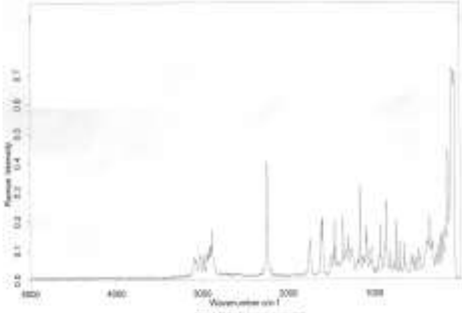
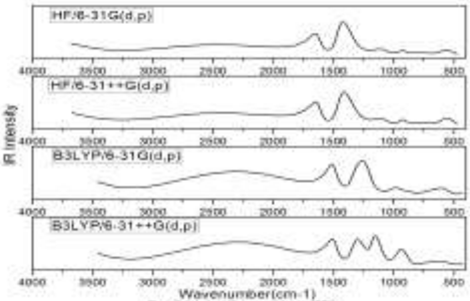


Figure 2. FTIR spectrum of sustiva(EFV)



[illegible]



[illegible]

Thermodynamic properties

Several calculated thermodynamic parameters are presented in Table 6. Scale factors have been recommended[17] for an accurate prediction in determining the zero-point vibrational energies and the entropy S. The variation in the ZPVEs seems to be insignificant. The total energies found to decrease with increase of the basis sets dimension. The changes in the total entropy of sustiva(EFV) at room temperature at different basis sets are only marginal.

DFT to a certain extent makes the frequency values smaller in comparison with the HF frequency data. Comparison of the frequencies calculated at HF/6-31, H/6-31++, B3LYP/6-31 and B3LYP/6-31++ with experimental values. The CH and NH stretching modes are expected to be observed at the high wavenumber region. The ν(CH) stretching bands are observed at the between 3324 and 3027 cm^{-1}. The very strong band at 2266 cm^{-1} may be assigned to the stretch mode of C≡C bonds. Now

Conclusions

The geometry of sustiva(EFV) was optimized with HF and DFT-B3LYP methods using 6-31G(d,p) and 6-31++G(d,p) basis sets. The complete molecular structural parameters and thermodynamic properties of the optimized geometry of the compound have been obtained from ab initio and DFT calculations. The bond order and atomic charges of the title molecule have been studied by both HF and DFT methods. The vibrational frequencies of the compound have been precisely assigned and analysed and the theoretical results were compared with the experimental vibrations. The energies of important MO's, absorption wavelength (λ_{max}), oscillator strength and excitation energies of the compound were also determined from TD-DFT method and compared with the experimental values. Thus the present investigation provides complete vibrational assignments, structural information and electronic properties of the compound which may be useful to upgrade the knowledge on sustiva(EFV).

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